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DEFENCE RESEARCH BOARD

DEPARTMENT OF NATIONAL DEFENCE
CANADA

AN INVESTIGATION OF THE MECHANISM OF THE OXIDATION, DECOMPOSITION, IGNITION AND DETONATION OF FUEL VAPORS AND GASES

-v. 13
PARTS I to XXX

1947 - 1957

by

R.O. KING
and
ASSOCIATES



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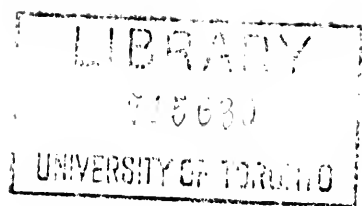
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FOREWORD

by

G.S. Field

Chief Scientist, Defence Research Board

This investigation was initiated in the Engine Section of the Air Ministry Laboratory, in the Physics Department of the Imperial College of Science, London, and was based on the development in 1925 of the Nuclear Theory of Ignition by Professor Hugh L. Callendar, Head of the Department. Mr. R.O. King, who had been a pupil of Callendar at McGill University, was put in charge of experiments related to the theory. Callendar ceased to be directly associated with the research in 1928 and died two years later. After 1928 King and his associates continued with the program, taking it with them to the Department of Mechanical Engineering, City and Guilds College, when the laboratory was transferred there in 1932. When King attained the Royal Air Force retiring age late in 1934, the laboratory was again transferred, this time to Farnborough.

The numerous research publications emanating from the Engine Section, Air Ministry Laboratory, had aroused general interest, and support was obtained for King to continue fuel research in Professor E.K. Rideal's Colloid Science Laboratory at Cambridge University. It was carried on there and in the Engineering Laboratory of the University until the outbreak of war in 1939. King then joined the Royal Observer Corps and also became an Air Raid Warden. He obtained permission to visit Canada in March, 1940, for family reasons, but when ready to return to England in June, 1940, transportation was not available.

At this stage Professor E.A. Allcut, Head of the Department of Mechanical Engineering, University of Toronto, who had kept in touch with the research carried on in England by King and associates, recommended King to Dr. C.J. MacKenzie for a position as inventions examiner in the National Research Council, Ottawa. King held this position until May, 1942, when he transferred to a similar position in the Royal Canadian Navy. Subsequently he was given charge of technical research projects and in August, 1944, was appointed to the position of Director of Scientific Research and Development. This position was held until 1947, when King transferred to the newly formed Defence Research Board. The Chairman of the Board, Dr. O.M. Solandt, had become interested in King's earlier work, and agreed to have him devote his whole time to writing up the results of the combustion research carried out in Cambridge but as yet unpublished. These papers were accepted for the *Canadian Journal of Research*, Section F, and constitute Parts I to IV of the series in this volume.

A continuation in Canada of the research was made possible by the interest of Professor Allcut in the nuclear theory of ignition, and the knock-testing engine in the heat engine laboratory was placed at the disposal of King for experiments with hydrogen as the fuel. As the results appeared to support the nuclear theory of ignition, the research was continued and greatly expanded in scope with the aid of successive extra-mural grants from the Defence Research Board until Professor Allcut retired in 1957. The thirty papers collected in this volume had by then been published in a National Research Council journal, before it ceased publication.

Papers describing later research have subsequently appeared in journals published in Canada, France, the United States, and England. A start has thus been made on a second volume.

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**THE OXIDATION, IGNITION, AND DETONATION OF
FUEL VAPORS AND GASES**

**I. A REACTION CHAMBER ADAPTED TO DETERMINE THE EFFECT OF
ANTIKNOCKS ON THE RAPID OXIDATION OF FUEL
VAPOR OF HIGH TEMPERATURES**

BY R. O. KING

THE OXIDATION, IGNITION, AND DETONATION OF FUEL VAPORS AND GASES

I. A REACTION CHAMBER ADAPTED TO DETERMINE THE EFFECT OF ANTIKNOCKS ON THE RAPID OXIDATION OF FUEL VAPOR AT HIGH TEMPERATURES¹

By R. O. KING²

Abstract

Slow combustion experiments by conventional laboratory methods show that metallic dopes such as the iron and nickel carbonyls and tetraethyl lead act as antioxidants in respect of the liquid paraffins present in engine fuel, the effect being especially marked at high temperatures. Such an effect failed to account for the results of certain engine experiments which could be interpreted only on the assumption that the metallic dopes *promoted* oxidation of the 'end gas' which is known to be the seat of knock.

The inconsistencies mentioned justified an investigation of conventional laboratory methods of measuring rate of oxidation. This led to the design of a small scale flow method reaction chamber in which a typical paraffin, such as pentane, containing iron carbonyl in small concentration and mixed with air in combining proportions could be oxidized to final products, without explosion, in a time of exposure of one second or less at temperatures rising to 700° C. Oxidation of the doped pentane was to the final products, carbon dioxide and steam, at all temperatures of reaction, rate of formation of carbon monoxide being barely measurable. On the other hand, the oxidation of pentane alone was accompanied by a profuse liberation of aldehyde, reaching a maximum rate at about 400° C. and giving a negative temperature coefficient of reaction over the range 400° to 500° C. Oxidation of the pentane alone occurred at a much lower rate, over the high temperature range, than when it contained iron carbonyl in the usual small proportion ($\frac{1}{2}$ of 1%).

The new reaction chamber was used less successfully in demonstrating the effect of tetraethyl lead to promote the oxidation of pentane owing to difficulties arising from the properties of lead. A measurable promoting effect was, nevertheless, obtained at all temperatures of reaction.

The text has been restricted to an account of the development of a novel type of reaction chamber and to oxidations of pentane necessary for the purpose. The chamber is of more general application.

Introduction

Conventional laboratory bulb or flow methods yield results for the effect of antiknock substances on the oxidation of hydrocarbons used as engine fuel that are difficult or impossible to reconcile with the behavior of the substances in the combustion space of an engine. The reacting mixture in the usual laboratory apparatus is oxidized slowly and explosion occurs generally in the temperature range 500° to 600° C., unless the tube or bulb is packed. In the engine, however, complete oxidation of the reacting mixture occurs in a small fraction of a second, and the last portion to burn, the 'end gas', is exposed to temperatures rising to 800° C., depending on the compression ratio used. It was considered that the behavior of fuels in the combustion space of an engine

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Contribution from Defence Research Board, Ottawa, Canada.

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might be interpreted in terms of laboratory oxidations if a reaction chamber could be designed to operate without explosion at temperatures above 500° C. and at the same time provide for complete oxidation of fuel vapor in a time comparable with that of an engine combustion period. Experimental work was undertaken accordingly and the degree of success attained is shown by results described in Sections III and IV.

Section I

REVIEW OF PUBLISHED EXPERIMENTAL RESULTS

The effect of antiknocks such as tetraethyl lead and the iron and nickel carbonyls on the oxidation of hydrogen and the numerous hydrocarbon constituents of engine fuel has been studied by many investigators. Conventional 'flow' or 'bulb' methods of experiment were used and explosion of the combustible mixture undergoing oxidation occurred at temperatures ranging from 500° to 600° C. unless the oxidation space were 'packed'. A complete review of the published experimental results would be lengthy and it will suffice to mention some of the more significant.

Pope, Dykstra, and Edgar (8) using an open tube flow method found that tetraethyl lead tended to inhibit the oxidation of *n*-octane at temperatures rising to 600° C.; inflammation occurred at higher temperatures.

Berl, Heise, and Winnacker (1) using a packed oxidation space were able to observe oxidations at 500° and 700° C. They obtained a more decided antioxidant effect for both tetraethyl lead and iron carbonyl in respect of pentane and hexane and, for example, reported that "by the addition of 1% of iron carbonyl under the conditions stated, the hexane remains practically unchanged; the oxygen remains unused".

Mardles (5) using the bulb method over the temperature range 230° to 320° C. found that tetraethyl lead tended to inhibit the oxidation of hexane at temperatures above 250° C. but promoted the effect at lower temperatures, and in a later publication (6) described experiments, made with a conventional flow method, showing an oxidation promoting effect for either tetraethyl lead or iron carbonyl in respect of hydrogen, methane, and ethane, irrespective of temperature. The inversion of the effect of metallic dopes was mentioned. No explanation was offered other than the quoted opinion of Moureau and Dufraisse that certain substances may act as oxidants in respect of some compounds and as antioxidants in respect of others.

Pidgeon and Egerton (7) using the bulb method at a constant temperature of 265° C. found the oxidation of pentane to be promoted when tetraethyl lead was freshly added; an inhibitory effect was observed after the metal of the dope became oxide.

The experimental work to which reference has been made, as well as a great deal of similar work not mentioned, was initiated in an endeavor to explain the antiknock effect of metallic dopes. Knock was regarded by many as due primarily to an oxidation process beginning with the formation of explosive

organic peroxides. The metal of the dope was supposed to destroy the peroxide or, in some way rather difficult to explain, interrupt chain reactions in which peroxides were essential links. The experiments were of the slow combustion type made generally at relatively low temperatures, and it is difficult to use the results as a foundation for a rational explanation of the effect of the dopes on combustion of the end gas in an engine which goes to completion in a small fraction of a second on exposure to temperatures extending to 800°C . The results are, however, in agreement in showing that, *in the conditions in which they were obtained*, the metallic antiknocks inhibit in varying degree the oxidation of the higher paraffins present in large proportion in commonly used engine fuel and mainly responsible for fuel knock. Some doubt was, however, cast on the validity of the antioxidant effect by finding that engine experimental results, not yet described, could be explained only by assuming that the dopes *promoted* oxidation in the related conditions.

The disagreement between laboratory and engine experimental results was discussed with Dr. F. H. Garner, Chief Chemist in England of the Standard Oil Development Co., and Prof. E. K. Rideal. The discussion led to arrangements being made to undertake a series of oxidation experiments, using new methods, in the Colloid Science Laboratory, Cambridge University. The experiments are described in succeeding sections, beginning with a description of the preliminary work required to recover typical oxidation results obtained by others and to devise a reaction chamber to reproduce in some degree the temperature and 'time of exposure' conditions prevailing in the combustion space of a carburetor engine.

Section II

PRELIMINARY EXPERIMENTS AND REACTION CHAMBER NO. 10

Oxidation research is usually conducted with a particular form of a conventional method to determine the characteristics of a number of substances. Thus it seemed that whether metallic antiknocks promoted the oxidation of some substances or inhibited the effect in others or reversed in effect on increasing temperature might depend on the form or scale of the laboratory apparatus. It was decided, therefore, to depart from the usual procedure by selecting one typical liquid paraffin for all the experiments and to confine the variables to the scale and design of reaction spaces.

The flow method of experiment was selected in preference to the bulb method for two principal reasons; (1) it permitted flexibility in the design and scale of the reaction space, and (2) it enabled samples of the reaction products to be withdrawn at any temperature for analysis. The experiments were made with mixtures of pentane vapor with air. The methods of fixing 'mixture strengths', of measuring rate of mixture supply to the reaction space, and of analyzing the oxidation products are described in the appendix.

Typical Oxidation Results (Mardles) for Pentane and Hexane, Conventional Flow and Bulb Methods

The results have already been mentioned, Section I. Those for pentane obtained by Mardles (6) using the flow method are shown graphically by Fig. 1. It will be noted that oxidation begins at about 220° C. and proceeds the more rapidly in the doped mixture until the temperature reaches 400° C. The graphs then cross and at higher temperatures the pentane is oxidized more rapidly than with tetraethyl lead added. The conditions of the experiment are not stated in the text of the reference quoted but it is known that

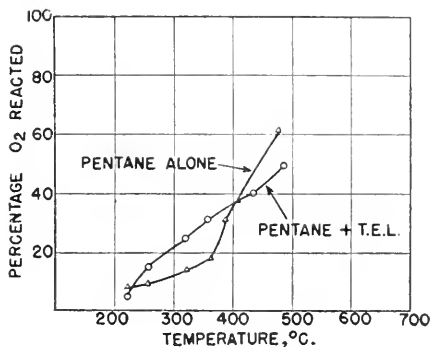


FIG. 1

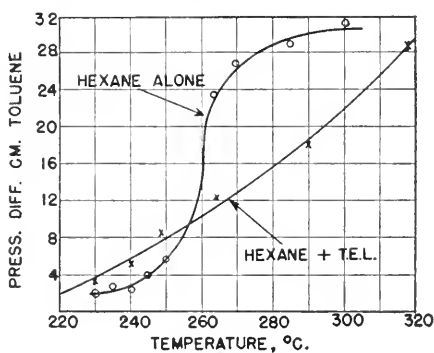


FIG. 2

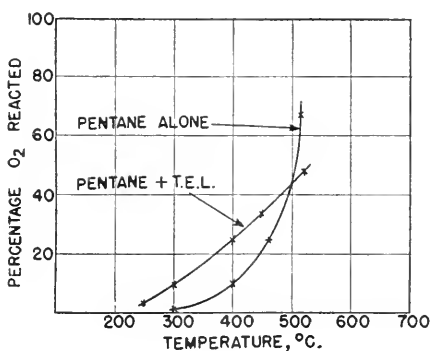


FIG. 3

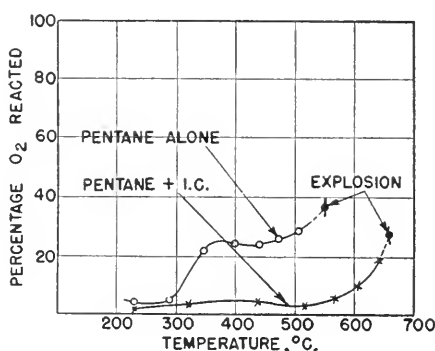


FIG. 4

FIG. 1. Pentane oxidation (Mardles). Tube method, $\frac{L}{D} = 25$. Flow = 16 cc. per min.

FIG. 2. Hexane oxidation (Mardles). Bulb method.

FIG. 3. Pentane oxidation (King). Tube method, $\frac{L}{D} = 32$. Flow = 150 cc. per min.

FIG. 4. Pentane oxidation (King). Tube method, $\frac{L}{D} = 6$. Flow = 150 cc. per min.

the rate of mixture supply was approximately 1 litre per hour, determined by 'counting bubbles'. The combustion tube was the usual hard glass variety, 12 mm. inside diameter supported horizontally in a tubular electric furnace 12 in. long. The mixture strength was determined by weighing a surface carburetor 'before and after'. Oxidation results obtained by Mardles (5) for

hexane, using the bulb method, are shown graphically by Fig. 2. Experimental details are given in the reference quoted. It will be noted that the reversal of the oxidation promoting effect of the tetraethyl lead is at approximately 255°C. , that is, 145°C. lower than observed for the pentane oxidation.

Effect of Changing Ratio of Length to Diameter of Combustion Tube

The Cambridge experiments were begun with the conventional set up of a combustion tube in a tubular electric furnace except that the furnace was exceptionally long (24 in.), the combustion tube being of Pyrex approximately 19 mm. internal diameter. The L to D ratio was, therefore, 32 instead of 25 as used by Mardles. The results of the oxidation of pentane alone and with the small addition of 0.25% by weight of tetraethyl lead are given by the graphs of Fig. 3. Comparing them with those of Fig. 1, it will be noted that the promoting effect of tetraethyl lead at relatively low temperatures was similar to that observed by Mardles but was maintained until the temperature reached 500°C. , that is, 100°C. higher. The experiments showed that the general characteristics of pentane oxidation already described in references given had been recovered. The next significant change in the reaction space was to *reduce* the L to D ratio to 6 by using a furnace 6 in. long and a combustion tube of 1.0 in. internal diameter. A Jena Supramax Glass tube was used in the expectation that it might be possible to carry oxidation to temperatures above 600°C. Temperatures were taken by a ring thermocouple of two junctions surrounding the combustion tube at the position of maximum temperature instead of by the usual arrangement of a couple enclosed in a silica sheath and fixed within the combustion space. The hot upper end of the combustion tube was closed by a stainless steel block provided with an outlet tube and surmounted by a safety cap which blew off in the event of an explosion and prevented damage. All joints were ground and remained tight.

The experimental results for pentane and pentane plus iron carbonyl oxidized in the short wide tube are given by the graphs of Fig. 4. They are quite remarkable in showing a greater *antioxidant* effect than obtained by any others in open combustion tubes—moreover, there was no reversal of the effect; it persisted from the temperature of initiation to that of explosion. Similar results were obtained when the pentane was doped with tetraethyl lead. It will be noted that the explosion temperature increased over 100°C. on adding the antiknock compound to the pentane although rate of reaction *diminished*. It is also noteworthy that with the relatively large diameter tube a 'hump' showing a slight negative temperature coefficient of reaction appears in the graph for the oxidation of pentane undoped. Similar results were obtained when combustion tubes of the same L/D but of different materials were used. The materials tried were nickel-steel, silica, and graphite.

The experiments seemed to have come to a dead end with an exceptionally complete verification of the antioxidant effect of tetraethyl lead in respect of a typical liquid paraffin and consequent confirmation of current theory that the antiknock effect is obtained accordingly. It was evident that if the

metallic antiknocks promoted oxidation at high temperatures, as seemed to be indicated by engine experiments, the effect could not be demonstrated by the use of conventional bulb or tube methods, and experiments were begun to design a new type of reaction chamber.

Considerations Leading to the Development of a New Type of Reaction Chamber

It is well known that deposits of metal and various metallic oxides remain on the interior surfaces of combustion tubes after oxidations of doped vapor mixtures. It is difficult to examine the residues in long narrow tubes. Short wide tubes possess the advantage that the deposit can readily be inspected and the nature of that seen at any position related to the corresponding temperature. Moreover, there were in short tubes, when heated, very steep temperature gradients from the middle to the ends, and if the tube were used in a vertical furnace, the deposits were left in fairly distinct successive bands of metal and colored oxides on cooling the furnace and stopping the flow of doped mixture. It was observed for all the short tubes used for the experiments mentioned above that after high temperature oxidations of pentane containing tetraethyl lead or iron carbonyl a metallic mirror, as a band, remained at or near the position of entry of the tube into the furnace. It seemed, therefore, that little if any of the metal yielded by the dope reached the position of maximum tube temperature if that were much above the temperature of decomposition.

Callendar's experiments (2, 3) with organometallic compounds in sealed tubes showed that the decomposition of tetraethyl lead was nearly complete at 215° C. and left a metallic mirror on the surface of the tube. Nickel carbonyl vapor decomposed readily at 150° C., the nickel being deposited on any available surface. Decomposition occurred solely on surfaces, not in the body of the vapor. The characteristic was, in fact, discovered by Mond many years earlier and remains the basis of the commercial method used to procure pure nickel. Callendar's experiments indicate that tetraethyl lead or iron carbonyl vapor when mixed with air and fuel vapor and passed through a heated combustion tube would not reach the seat of a high temperature reaction before being decomposed at a lower temperature to yield metal which would be deposited on contact surfaces and oxidize rapidly in the conditions.

In accordance with the above mentioned considerations, experiments were made to determine the position of iron carbonyl decomposition in a 1 in. diameter Pyrex tube set horizontally in a 6 in. tubular furnace. A pentane-air mixture in combining proportion was passed into the tube at the rate of 150 cc. per min. through a 6 mm. Pyrex inlet tube as shown by Fig. 5. The pentane contained iron carbonyl in the concentration of 0.5%. The reacting mixture was allowed to flow for two hours while the temperature indicated by a ring thermocouple surrounding the tube at the middle of the furnace was maintained at 400° C. The tube was used in the horizontal position because the deposits of metal and oxides give a better indication of the path of the mixture than when the tube is vertical and the deposits appear as bands.

The traces remaining on the tube on completion of the experiment were photographed and are shown in elevation and plan by *A* and *B*, Fig. 5. They indicate the path of the mixture in the tube to be as shown by *C* of the same figure. The entering mixture, being relatively cool, falls in a stream and leaves a small iron mirror where it strikes the bottom surface. It is then heated by contact with the glass and rises through the relatively cool mixture in the entrance end of the tube, the rising stream being divided by the small mixture admission tube on which deposits of red oxide are left. The stream then strikes the top of the tube receiving more heat and moves toward the middle. The markings show, however, that it falls away from the top surface, presumably when it reaches mixture of higher temperature and consequently lower density.

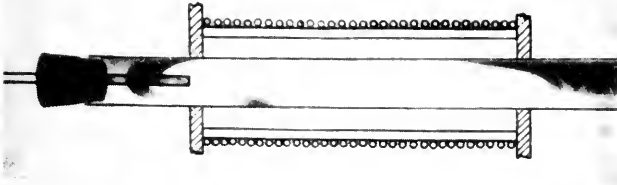
It appears that when gaseous mixtures at room temperatures are admitted to the cool end of a combustion tube a heating eddy is formed. Similarly a cooling eddy is formed when the mixture leaves through a central outlet.

Except for the small iron mirror already mentioned, all the deposits from the eddy in the entrance end were red oxide and apparently nothing but that substance passed through the middle part, which is the position of maximum temperature and generally assumed to be that of the greatest degree of oxidation activity. That it did pass through was shown by the heavy deposit of oxide from the exit eddy.

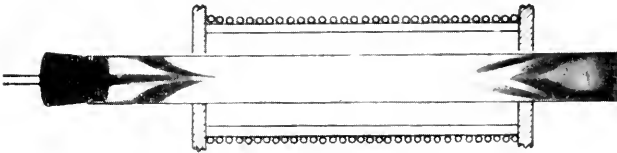
The experiment was of general interest in showing that 'exposure time' as usually calculated is in error, but the point of immediate interest was the demonstration that the metal of the dope in a gaseous mixture passed through a conventional type of combustion tube tends to be deposited on surfaces at or near the entrance of the heating furnace as the temperature is raised. The deposition would be expected to increase with the magnitude of the entrance eddy, which in turn increases with increase in the tube diameter or a decrease in L to D ratio. Thus an explanation is afforded for the experimental results of Figs. 1, 3, and 4, showing that the antioxidant effect of the dope increases as the L to D ratio of the combustion tube diminishes. Obviously the effect of metallic dope on oxidation, as observed in engine experiments, would be reproduced in laboratory experiments only if the dope were introduced into the actual reaction space before being decomposed. The experiment showed very definitely that this condition cannot be met with the conventional straight-through combustion tube arrangement.

Reaction Chamber No. 10

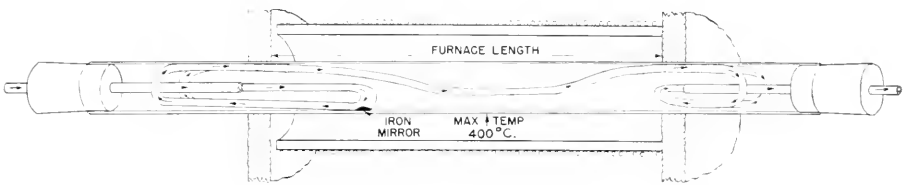
The problem of designing a reaction chamber suitable for ensuring that the metal yielded on the decomposition of the dope content of pentane is present at the position of a high temperature reaction in a pentane-air mixture was not easy of solution. Reasonable finality of design was achieved with Reaction Chamber No. 10, illustrated by Fig. 6, *A* and *B*. *A* shows the complete arrangement as set up in an electric furnace and *B* an enlarged section of the reaction chamber and adjacent parts.



A. Side view of combustion tube.



B. Plan view of combustion tube.



C. Indicated path of a filament of the mixture.

FIG. 5. Showing the effect of heat convection on the flow path of a doped pentane-air mixture through a conventional combustion tube and the very small area on which metal is deposited as a mirror.

It will be seen by reference to the figure that the reaction chamber is an inverted cup formed in the end of a tube which is contained within another of sufficiently large diameter to provide an annulus about 1.0 mm. wide for the escape of gas from the reaction space. The tubes may be of any material suitable for use at high temperatures, provided the decomposition and oxidation products of metallic dope will adhere to the heated surfaces. The lower end of the cup is nearly closed by an asbestos cement washer, fitting closely

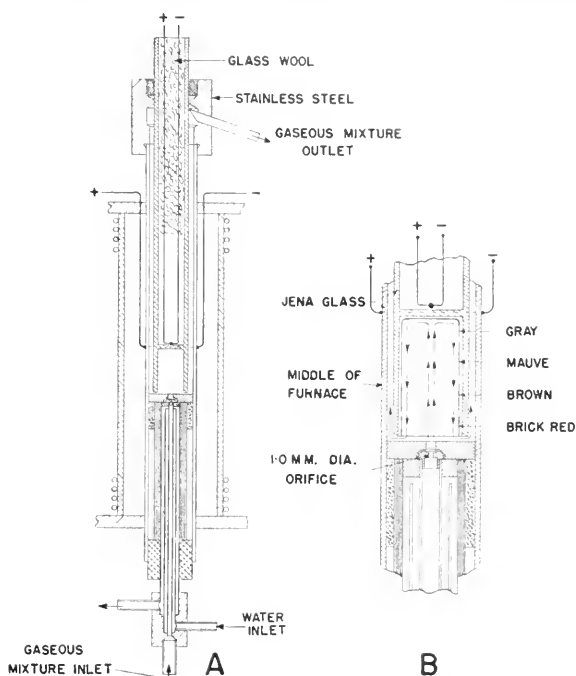


FIG. 6. General arrangement of Reaction Chamber No. 10 in electric furnace and enlarged section of chamber.

in the outer tube and having a small central hole through which the gaseous reacting mixture is admitted as a jet from a small orifice in the top of a water cooled inlet device. It is important that the opening from the reaction chamber into the annulus should be no greater than required to avoid appreciable resistance to the gas flow. The orifice was usually 1.0 mm. diameter but must be of such a size that the jet created by the mixture passing through it will maintain a streamline form until it strikes the top of the reaction chamber; preliminary experiment showed that in the circumstances metallic dope in the reacting mixture does not decompose until contact is made with the surface. The arrows, Fig. 6, B, show the path of the reacting mixture from the admission orifice, through the reaction chamber to the annulus and thence upward to the outlet tube at the upper end of the apparatus.

The reaction chamber as used for most of the experiments was 12 mm. diameter and 22 mm. long, the volume being 2.5 cc. The reacting mixture

was generally supplied at the rate of 150 cc. per minute, that is, sufficient to fill the chamber 60 times per minute. The reaction space of a four stroke internal combustion engine is filled at the same rate when the speed is 120 r.p.m.

The reaction chamber was supported in an electric furnace and thermocouples for temperature measurement arranged as shown by the diagrams, Fig. 6. A pair of thermocouples made up of a wire ring, half iron and half constantan, giving junctions at opposite ends of a diameter, was used to measure 'outside' or furnace temperature. The ring fitted easily over the outer glass tube and the connections leading to an indicator are shown by the figure. A single thermocouple was used to measure the 'inside' temperature on the top of the reaction chamber. The thermocouples and the related indicators were supplied by the Cambridge Instrument Company.

Jena Supramax glass reaction chambers were used for determining the effect of iron carbonyl on the oxidation of pentane. This variety of glass remains hard at temperatures exceeding 700°C . and resists attack by metallic oxides at lower temperatures. Decomposition and oxidation products of the carbonyl do not adhere to the glass until after a doped pentane-air mixture has been passed through the chamber for a short time while the temperature is maintained at about 700°C . The preliminary treatment effects a slight roughening of the glass. The chamber cannot properly be used for pentane oxidations after use with mixtures containing dope unless it is cleaned with hydrofluoric acid and washed with steam.

The device for ensuring that unheated doped pentane-air mixture entered the reaction chamber is shown at *A* and *B*, Fig. 6. The device was, of course, a cold body with the upper part adjacent to the high temperature reaction chamber and it was necessary to insulate it as thoroughly as possible. The insulation comprised the asbestos cement washer already mentioned and, in addition, the body of the device was wrapped with layers of asbestos paper and the upper part wound with asbestos yarn to form a plug fitting tightly in the outer tube. The insulation arrangements are illustrated by *B*, Fig. 6. The water cooled inlet device may have caused some cooling of the lower end of the reaction chamber, but at least partial compensation was obtained by adjusting the apparatus in the furnace to bring the top of the reaction chamber slightly above the position of maximum temperature. The diagram *A*, Fig. 6, is in error in showing the chamber below the position of maximum temperature. In any event, reacting mixtures, passed through the chamber at much higher rates than generally used for laboratory experiments, could be raised to the temperatures, about 700°C ., required for complete oxidation.

The upper ends of the tubes of the reaction chamber became extremely hot when oxidation temperatures ran to 700°C . Rubber connections could not be used, and a special device illustrated by *A*, Fig. 6, was found to be satisfactory. The upper end of the outer glass tube was ground flat and made a joint on a flat surface of the stainless steel block. The inner glass tube passed through the block, in which a recess in the nature of a 'stuffing box' was turned. The recess was packed with asbestos.

Section III

TRIALS OF REACTION CHAMBER NO. 10

A combining proportions mixture of air with pentane containing iron carbonyl in the concentration of 0.5% by volume was supplied to the chamber at the rate of 150 cc. per min. and samples of oxidation products taken for analysis while the temperature was raised by steps to 700° C. The upper graph of Fig. 7 shows the rate of oxygen reacted plotted against temperature.

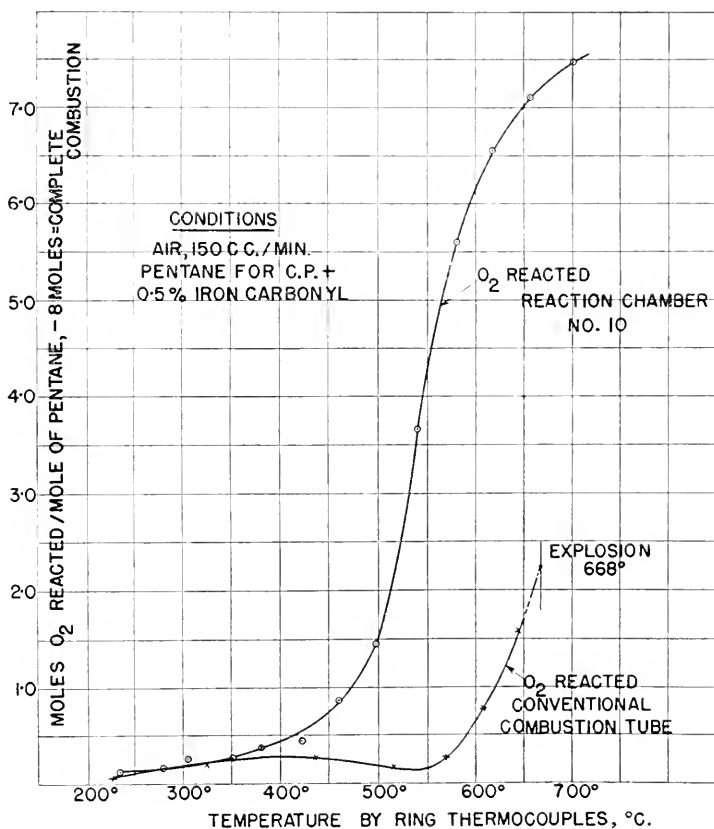


FIG. 7. Rate of oxidation of a doped pentane-air mixture in Reaction Chamber No. 10 compared with the rate in a conventional combustion tube.

The lower graph of the figure shows the rate at which oxygen was reacted when a similar mixture was passed through a conventional open combustion tube, 25.0 mm. diameter in a 6 in. furnace, at the rate of 150 cc. per min., as described in Section II with reference to Fig. 4.

The design of the reaction space constituted the sole difference between the conditions of the two experiments but the oxidation results differed in a somewhat remarkable manner, thus, (a) oxidation in Reaction Chamber No. 10 occurred at an extremely high rate especially at temperatures above 500° C.

At 600° C. the rate was 6.2 moles of oxygen reacted as compared with 0.7 moles in the conventional combustion space having a volume 30 times greater if the length of tube inside the furnace is as usual regarded as reaction space, (b) the doped mixture did not explode in Reaction Chamber No. 10 in spite of the high rate of reaction, reaching substantial completion at 700° C. On the other hand a similar mixture in the combustion tube exploded at about 668° C. and the last sample taken before the event showed that only 1.6 moles of oxygen had reacted. Rates of oxygen reacted, and of carbon oxides formed, in Reaction Chamber No. 10 are shown by the graphs of Fig. 8. It will be noted that carbon monoxide formation was inappreciable, indicating that oxidation was to the final products, carbon dioxide and steam, at all temperatures of reaction.

The colors of the deposits on the surface of the Reaction Chamber were as shown at *B*, Fig. 6. They appeared in distinct bands beginning with gray (iron) which covered the top of the chamber and extended a short distance down the wall, then mauve, brown, and finally brick red. The colors show the progress of oxidation of the iron in the carbonyl as it passes from the top to the bottom of the reaction chamber.

Oxidation of Pentane (Undoped) in Reaction Chamber No. 10

The pentane-air mixture in combining proportions failed to explode when passed through the chamber although the temperature was raised to 660° C. The mixture was supplied as before at the rate of 150 cc. per min. The rates of oxygen reacted are given by Graph *A* of Fig. 9. Graph *B* for doped pentane, reproduced from Fig. 7, is shown for comparison.

It will be seen by reference to the graphs that the pentane alone is oxidized at a greater rate than when doped, over the temperature range 330° to 500° C. This is the temperature range of aldehyde formation and the graph shows what became known in subsequent work as the 'aldehyde hump' with a marked *negative* temperature coefficient of reaction. The rates of formation of carbon oxides are shown by the graphs of Fig. 10 and are significant of aldehyde formation. It is of interest to compare them with the graphs of Fig. 8, which show an almost complete absence of carbon monoxide in the oxidation products of the doped pentane.

The temperature region above 500° C. is of special interest because one of the objects of the investigation was to provide means for working in the temperature range of the 'end gas' in an engine. The very great effect of the carbonyl to promote oxidation at high temperatures will be noted. Thus, referring to Fig. 9, at 600° C. with 0.5% of iron carbonyl in the pentane, 6.2 moles of oxygen were reacted to form carbon dioxide and steam whereas without the carbonyl only 1.4 moles of oxygen were reacted and oxidation was not to final products.

Inside and Outside Temperatures

The ring thermocouples surrounding the outer tube of the reaction chamber would be expected to indicate a higher temperature than the couple resting on

the top of the reaction chamber and indicating more nearly the temperature of the chamber. Outside temperatures were, however, used for plotting results, merely to continue the practice begun before the development of a separate reaction chamber within an outer tube.

When pentane alone was oxidized in the chamber, outside temperature was the higher by 17°C . at the beginning of the experiment. The difference reached a maximum of 25°C . at reaction temperatures of about 500°C . and then diminished to again become 17°C . at 600°C . The initial difference was again about 17°C . in the experiment with doped pentane, as would be expected. A maximum difference of 20°C . occurred at 400°C . and thereafter diminished to become 13°C . only at 700°C .

The inside thermocouple rested on the top surface of the reaction chamber and the temperature differences given are consistent with the view that reaction occurred mainly on the upper surface of the chamber. The temperature differences show that the rate of heat liberation was the greater when doped pentane was oxidized, as would be expected.

Section IV

OXIDATION OF PENTANE DOPED WITH TETRAETHYL LEAD IN REACTION CHAMBER NO. 10

It is evident from the experiments described in Sections II and III that the rapid oxidation in Reaction Chamber No. 10, of pentane doped with iron carbonyl, was a surface effect probably occurring mainly on iron deposited on decomposition of the carbonyl. The iron so obtained covered a considerable part of the reaction chamber surface as shown at *B*, Fig. 6, and mentioned earlier. An equal area of metal would not be expected when using lead dope because the surface of the chamber must be heated to a temperature far above the melting point of lead (327°C .) if the pentane is to be oxidized at an appreciable rate. Moreover, lead oxidizes with great rapidity in the conditions and the oxides tend to dissolve in glass at high temperatures. Thus after passing a pentane-air mixture doped with tetraethyl lead through the glass reaction chamber at high temperatures the wall surface remained smooth but discolored. There was, however, on the top surface a slight metal coating in the form of a disk about 4.0 mm. diameter covering the spot where the jet of cool reacting mixture impinged. The disk was surrounded by a ring of orange colored oxide about 1.0 mm. wide. Beyond it was a wider ring of light yellow grading off to chalk white. Similar deposits were procured in some quantity from other experiments and the chalk white substance identified as a lead oxycarbonate, $\text{PbO} \cdot 2\text{PbCO}_3$. The yellow color indicated that some PbO remained in the oxycarbonate.

In spite of the difficulties it was possible by using a steel reaction chamber to obtain conditions in which tetraethyl lead acted to promote the oxidation of pentane at temperatures ranging to 650°C ., although the effect was much smaller than observed for iron carbonyl, as would be expected in view of the

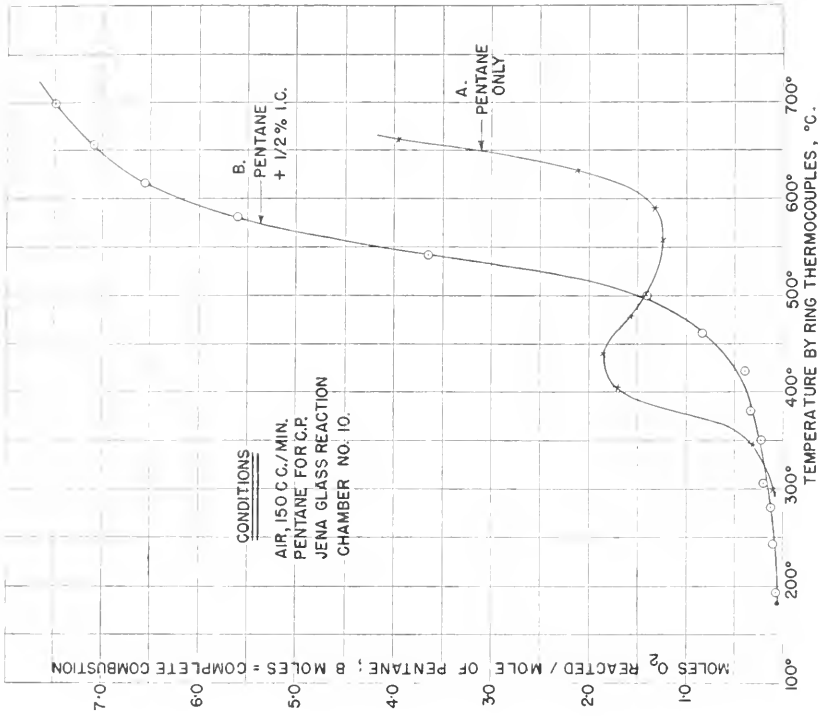


FIG. 9

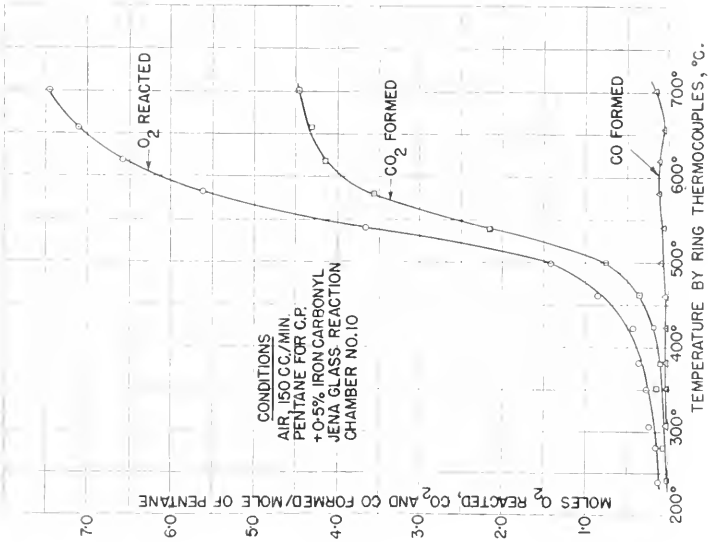


FIG. 8

FIG. 8. Rates of carbon monoxide and carbon dioxide formation when doped pentane is oxidized in Reaction Chamber No. 10.
FIG. 9. The effect of iron carbonyl on the oxidation of pentane in Reaction Chamber No. 10.

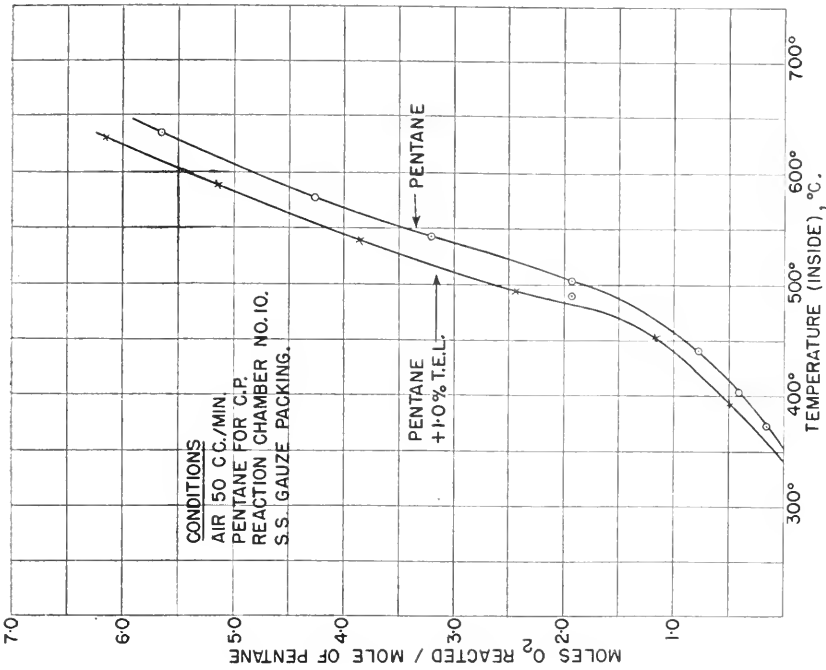


FIG. 11

FIG. 10. Rates of carbon monoxide and carbon dioxide formation when pentane (undoped) is oxidized in Reaction Chamber No. 10.

FIG. 11. Effect of tetraethyl lead on the oxidation of pentane in Reaction Chamber No. 10 (packed).

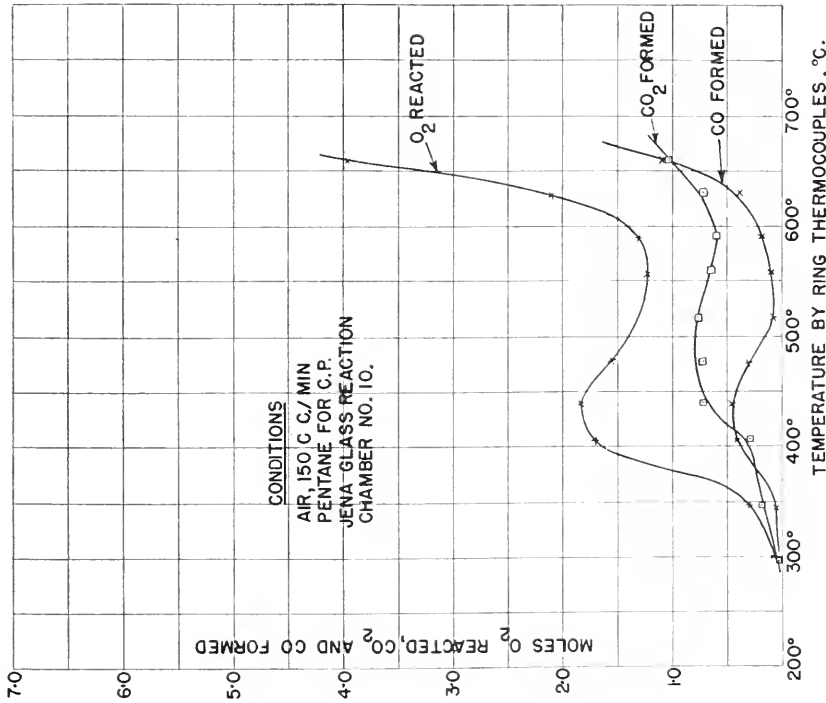


FIG. 10

circumstances mentioned. The design was similar to that of the Jena glass chamber illustrated by Fig. 5, but a roll of stainless steel gauze was placed in the reaction space to increase the area of surface on which deposition of metal from the dope might occur. The jet of entering mixture passed into and through a central hole in the roll of gauze.

The results of oxidations of pentane alone and pentane containing tetraethyl lead in the concentration of 1.0% are given by the graphs of Fig. 11. Temperatures are as given by an 'inside' thermocouple because the 'ring' thermocouples could not be used in contact with a steel tube. Referring to the graphs it will be noted that the 'aldehyde hump' with a negative temperature coefficient of reaction has disappeared and that rate of reaction is the higher for the doped pentane at all temperatures to 650° C. with 75% of the oxygen reacted. At the temperature of 500° C. rate of oxygen reacted increased from 1.8 to 2.6 moles (44%) on the addition of the dope—the difference remained fairly constant as the temperature increased to 650° C. The oxidation promoting effect of the tetraethyl lead over the high temperature range is of special interest because it is the opposite to that obtained in conventional combustion tubes. The reacting mixture was supplied to the reaction chamber at the rate of 50 cc. per min., so moles of oxygen reacted represent a lower rate of reaction than when the rate of supply was 150 cc. per min. as for the iron carbonyl experiments. The lower rate of reaction and the lack of an aldehyde hump are attributed to the effect of packing the reaction chamber.

Section V

REVIEW OF THE EXPERIMENTAL RESULTS

Although the temperature and time of exposure conditions in an engine combustion space are approached in Reaction Chamber No. 10, an important other condition is not obtained. Thus the end gas in the engine is raised to an extremely high temperature* by compression while contained by relatively cool walls, except for the exhaust valve surface, but the mixture passing through Reaction Chamber No. 10 is raised in temperature by contact with the heated walls.

The metal deposited on the relatively cool walls of the engine cylinder could persist as such for a longer time in an oxidizing atmosphere than when deposited on the hot walls of Reaction Chamber No. 10. This feature is illustrated by the difficulty of maintaining lead as compared with iron on the surface of the reaction chamber. The catalytic activity of any metal coating would, however, be expected to increase with rise in temperature. Thus the upper graph of Fig. 7, for the oxidation of pentane doped with iron carbonyl, shows a gradually increasing rate of oxidation as the temperature rises from 200° C., but over the range 500° to 580° C. the rate increased from 1.5 to 5.6 moles, that is, about 400% for a rise of 80° C. The rate of change of reaction

* It is calculated from reliable indicator diagrams that when combustion is 90% complete in an engine, the temperature of the remaining unburnt mixture (end gas) has been raised by compression to 670° C. when the compression ratio is 4 to 1, and to 800° C. when it is 8 to 1.

was in fact so great, as indicated by the slope of the graph, that a reliable observation at 540°C. was obtained only after very careful stabilization of temperature and other conditions. The rate of change of oxidation diminishes over the temperature range above 580°C. merely because reaction tends to completion.

The experiments with Reaction Chamber No. 10 indicate that the oxidation of doped pentane is a heterogeneous reaction. If, contrary to accepted theory, the oxidation of pentane occurs similarly, aldehyde formation depending merely on the nature of the contact surface, a simple fundamental explanation would become available for all the phenomena associated with the effect of metallic dopes on combustion in the engine. It is hoped that experiments made accordingly can be described in a subsequent publication.

Acknowledgments

The experimental work described in this paper is part only of that carried out in the Colloid Science Laboratory, Cambridge, with the co-operation of Prof. E. K. Rideal and Dr. F. H. Garner.

The laborious and accurate gas analyses work was undertaken by Mr. R. R. Davidson, Emmanuel College, Cambridge, to whom credit is given for improvements in methods of using the Ambler apparatus.

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APPENDIX

Methods of Measurement

Extended experimental work on oxidation, using a flow method, requires analyses of hundreds of gas samples and convenient methods of supplying reacting mixtures of known composition at known rates. The methods used for the experiments of Sections II to IV will be described briefly in order to indicate that measurements were made with sufficient accuracy; a detailed description is unnecessary for present purposes and would require separate publication.

Gas Analysis

When pentane-air mixtures flowing through a conventional combustion tube are raised to high temperatures, such oxidation as may be obtained is

accompanied by the liberation of clouds of smoke, indicating that the gas issuing from the reaction space would contain some products of decomposition such as methane, hydrogen, and unsaturateds as well as those desired, namely, products of oxidation. A complete analysis would, therefore, be tedious and difficult. When, however, similar mixtures were passed through Reaction Chamber No. 10, oxidation generally occurred with great velocity at high temperatures and the course of the reaction could then be followed by determinations of oxygen reacted, and of carbon monoxide and carbon dioxide formed, using an Ambler gas analysis apparatus.

Gas Samples:—The gases from the reaction chamber were passed through at least two condensers, the first cooled by water-ice and the second by solid carbon dioxide in acetone. The uncondensed gas could then, in the absence of appreciable pyrolysis, be assumed to contain only nitrogen, oxygen, and carbon oxides. Samples enough for two analyses were taken in 15 cc. test tubes by mercury displacement and the tubes transferred while still in the mercury trough to individual 10 cc. crucibles and stored in racks.

'Pentane' and Combining Proportions Mixtures:—The pentane, supplied by the Anglo-American Oil Company, was procured by fractional distillation from aromatic free petroleum spirit; distillation range 30° to 40° C., 60% being recovered below 33.5° C. The molecular composition was taken to be C_5H_{12} and, assuming that air contains 20.9% of oxygen, the combining proportions mixture as admitted to the reaction chamber contains the gases in the proportion of 1 mole of pentane to 8 moles of oxygen to 30.3 moles of nitrogen. The accuracy of analysis depends on the proportion of nitrogen in the reacting mixture being known and if the reacting mixture contains oxygen and pentane in correct combining proportions, then when oxidation is *complete*, nitrogen and carbon dioxide only should be found in the gas collected from the condenser, a result which was sometimes achieved.

Air Supply:—The air supply was obtained from the usual high pressure storage cylinders and was, therefore, nearly dry. The air discharged through two-stage regulators (British Oxygen Co.) and any desired rate of flow could be kept nearly constant. The air passed from the regulator through long glass capillary tubing and rate of flow was determined by pressure difference, the capillaries being calibrated *in situ* by the displacement method.

Pentane Supply:—Pentane was required at a small constant rate. The rate is 0.470 gm. per hr. for a combining proportions mixture with air at 20° C. supplied at the rate of 100 cc. per min. The pentane was supplied at any desired rate by a Rideal microdoser (4).

Carburetor:—The very simplest form only is required, especially with the more volatile fuels. The carburetor used for the experiments is illustrated, reference (4), and to ensure thorough mixing of the air and pentane vapor a length of about 3 ft. of $\frac{1}{4}$ in. diameter glass tubing was interposed between the carburetor and the reaction chamber.

**THE OXIDATION, IGNITION, AND DETONATION OF
FUEL VAPORS AND GASES**

**II. THE EFFECT OF FLOW CONFIGURATION ON THE VELOCITY OF
THE OXIDATION REACTION IN PENTANE-AIR MIXTURES**

By R. O. KING

THE OXIDATION, IGNITION, AND DETONATION OF FUEL VAPORS AND GASES

II. THE EFFECT OF FLOW CONFIGURATION ON THE VELOCITY OF THE OXIDATION REACTION IN PENTANE-AIR MIXTURES¹

BY R. O. KING²

Abstract

Reynolds Numbers for the commonly used rates of flow of a reacting mixture through a conventional combustion tube are far below the critical value. The laminar flow to be expected accordingly is disturbed by convection currents when the tube is heated and flow configuration depends on such factors as ratio of length to diameter and temperature gradients but can be varied by creating local differences of flow velocity within a uniformly heated reaction space such as reaction chamber No. 10 described in Part I. The effects on reaction velocity of the factors mentioned have been determined by experiments described in this part. The results indicate that the velocity of a heterogeneous reaction is determined by flow configuration, that 'packing' does not distinguish between homogeneous and heterogeneous reactions and that the oxidation of pentane, taken as a typical hydrocarbon, is a heterogeneous reaction.

Section I

INTRODUCTION

It was shown by experiments described in Part I (2) that the dimensions and design of reaction spaces were major factors affecting reaction velocity. These factors determine flow configuration and can be varied to produce laminar or turbulent flow or a mixture of both types.

When gas flow through a tube is laminar, velocity is regarded as zero in the layer adjacent to the surface and as increasing in successive layers to a maximum at the longitudinal axis. The average velocity is directly proportional to pressure difference and the energy required to maintain the flow is expended in overcoming viscosity. Laminar flow breaks down to turbulent motion when the velocity through the tube reaches the critical value of the Reynolds Number. Turbulent motion tends to fill the tube and velocity becomes nearly uniform over a cross section normal to the longitudinal axis and is proportional to the square root of pressure difference. The energy required to maintain the flow increases accordingly and is expended in large part in overcoming friction between the wall and the gas stream. The friction gives rise necessarily to a scouring effect.

The flow configuration in an unheated combustion tube can now be considered. A glass tube 2.31 cm. internal diameter was used for many oxidation experiments, air being supplied at the rate of 100 cc. per min. The average velocity is then 0.4 cm. per. sec. and the Reynolds Number 6.58. The critical value for ordinary glass tubing is about 2300 in any self-consistent system of units, thus it would be necessary to increase the air supply in the ratio

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2300/6.58, that is, to about ³⁵⁰⁰~~3500~~ cc. per min. to initiate what is generally described as turbulence. It would be difficult though not impossible to arrange an oxidation experiment accordingly. Alternatively, a local effect on flow configuration equivalent to that obtained when the Reynolds Number exceeds the critical value can be obtained by methods described in succeeding sections.

The flow method of oxidation and mixtures of pentane in combining proportions with air, with one exception, were used for the experiments. The 'pentane' was similar to that used for the experiments of Part I and has been described in the appendix to that part. The experimental results for oxidations are given by graphs, moles of oxygen reacted being plotted against temperature. Methods of measuring air and pentane supply and of analyzing oxidation products were as described in the appendix to Part I.

Section II

FLOW CONFIGURATION AND RELATED REACTION VELOCITY IN NARROW (PACKED) SPACES

The ratio of surface to volume is sometimes increased by packing an open combustion space with fragments of the material of the wall, or with lengths of small tubes of the material if a measurable change in the ratio of surface to volume is required. A sufficiently narrow annulus between two coaxial tubes constitutes a packed combustion space and the arrangement facilitates changes of flow configuration. Tubing of invariable diameter and wall thickness is required for an annulus of uniform width over any considerable length and cannot be obtained in glass except by grinding to size. Recourse was had, therefore, to cold drawn steel tubing, which is of uniform inside and outside diameter, and can be had from stock in great variety of size and gauge. Steel possesses the further advantage that wall temperatures can be measured by the use of thermocouples electrically welded into the tubes at desired positions. Mild steel annular reaction spaces of two designs are illustrated by Fig. 1. Design A provides a straight through annulus and Design B a double annulus with communicating orifices in the partition wall at the position of maximum temperature.

Flow Configuration, Single Annulus

Both tubes were 20 gauge (0.036 in.) wall thickness. The inside diameter of the outer tube was 1.1155 in. and the outside diameter of the inner tube 1.0000 in. The width of the annulus was therefore 0.05775 in. or 1.47 mm. and the area of cross section 1.24 cm². Gas supplied at 100 cc. per min. would pass through the annulus with a velocity of 1.34 cm. per sec., and at the temperature of supply the flow could not be other than laminar. When, however, the tubes are heated in an electric furnace, the outer attains a higher temperature than the inner and if the tubes are vertical the layer of gas adjacent to the outer wall must rise at a somewhat greater velocity than that adjacent to the inner and cooler wall. Relative motion of the two layers becomes greater

than prevails in purely laminar flow and small eddies form between them. The path of the gas being annular in cross section, the eddy motion would be expected to take the form of vortex filaments moving upward with the gas flow.

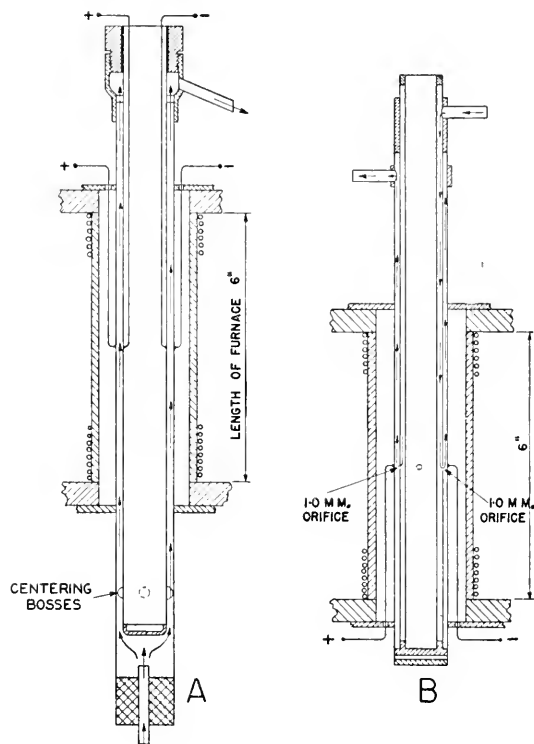


FIG. 1. Annular combustion tubes (steel).

A. Single straight through annulus.

B. Double annulus with four orifices in partition.

Flow Configuration, Double Annulus

The double annular combustion space is so arranged that gas entering the inner annulus at the upper end descends to the position of maximum temperature to pass through four 1.0 mm. orifices, equally spaced around the partition wall, into the outer annulus and thence to the exit at the upper end of the apparatus. The design provides an annular combustion space of the same width as that of Arrangement A and of the same length within the furnace but having means for changing flow configuration at the position of maximum temperature. The flow path of the reacting mixture is otherwise similar to that in the single annulus except for the dead space between the cool end and the ring of orifices. The space might have been filled but after preliminary experiments demonstrated the effect of flow configuration on reaction velocity, it appeared that oxidation in the space would be inappreciable as compared with that in the path of the moving mixture. The area of cross section of the inner annulus was 1.32 cm^2 , that is, only slightly greater than the 1.24 cm^2 .

of the outer annulus; flow velocities would, therefore, be approximately equal. The flow configuration may be taken as similar to that in the single annulus except at the position of maximum temperature where the reacting mixture passes through the four orifices. The total area of cross section of the orifices is 0.031 cm^2 and, that of the annulus being 1.24 cm^2 , gas velocity through the orifices is 40 times greater than the average through the annular spaces. The relatively high velocity creates a purely local disturbance, breaking down the nearly laminar flow and producing a scouring effect over a small surface area.

Preliminary 'Packing' Experiments

Reaction spaces with steel walls are not generally used for laboratory oxidations and the effect of 'packing' was determined by oxidations in the outer tube used alone and in the single annulus of which the same tube forms the outer wall. The inside diameter of the outer tube was 1.1155 in. and, the length within the furnace being taken as reaction space, surface to volume ratio was 1.49. The ratio for the annular reaction space was 13.6 on the same basis. Pentane-air mixtures in combining proportions were supplied at 200 cc. per min. for both experiments. Reaction velocities are given by the graphs of Fig. 2. It will be noted that reaction in the annulus did not begin

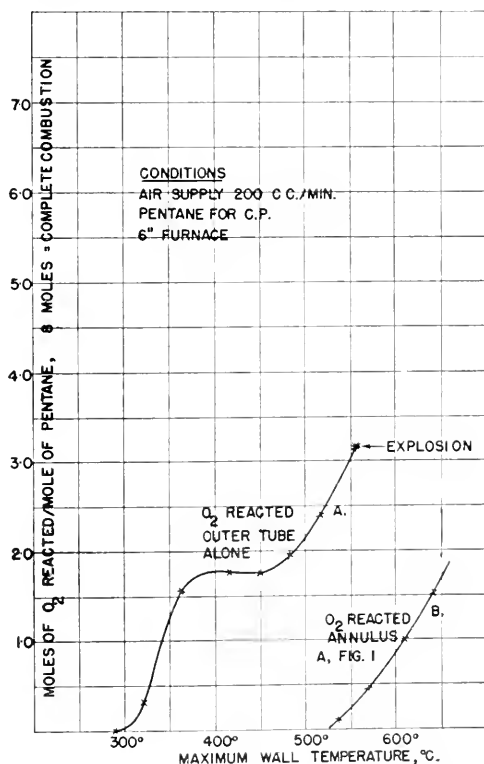


FIG. 2. Graph A. Reaction rates with convection currents.
Graph B. Reaction rates with nearly laminar flow.

at a measurable rate until the temperature reached 535°C ., which is beyond the range over which partial oxidation products are usually obtained. The final sample was drawn at 640°C . when the tubes were red hot but explosion did not occur. On the other hand oxygen was reacted at an easily measurable rate in the wide tube at 310°C . The rate increased rapidly over the temperature range 310° to 400°C . giving the familiar hump on the graph associated with profuse formation of aldehyde as described in Part I. The reacting mixture exploded at 560°C . The reaction velocities shown by the graphs of the figure *taken at their face value* show that increase in the ratio of surface to volume leads to a reduction in reaction velocity and support the generally accepted view that reaction chains can be initiated or broken on surfaces. It will be shown, however, by experiments described in succeeding sections that the apparent wall effect to reduce reaction velocity is due to flow configuration, not to the breaking of reaction chains.

Reaction Velocity in the Single Annulus as Affected by Change in Flow Configuration Due to Changing Temperature Difference Between Walls

The single annular combustion tube was set up in a vertical furnace as shown at A, Fig. 1. Pentane-air in combining proportions was admitted at the lower end at the relatively low rate of 40 cc. per min. in order that rates of reaction might be greater than determined for the higher rate of 200 cc. per min. The thermocouples at the position of maximum wall temperature indicated that over the range 400° to 600°C . the temperature of the outer tube was on the average 23°C . higher than that of the inner tube. The difference was 27°C . at 400°C . and 18°C . at 600°C . The average temperature difference was reduced to 20°C . by filling the inner tube loosely with asbestos-magnesia to eliminate convection currents.

Rates for reaction for the two conditions are given by Graphs A and B of Fig. 3. It will be noted that the higher rate of reaction, Graph A, is obtained for the greater temperature difference between the walls although the average temperature is the lower. The 15% increase in temperature difference would increase the *relative* velocity of the ascending layers of gas and consequently the size and velocity of the intermediate vortex filaments and the effect on reaction velocity shown by the graphs is quite remarkable. Thus, at 500°C . outer wall temperature rate of reaction increased from 1.8 to 2.4 moles of oxygen or 33% on increasing the temperature difference between the walls by 15%; at 550°C . the rate of reaction increased by 25%.

Reaction Velocity in the Double Annulus as Affected by Change of Flow Configuration at the Position of Maximum Temperature

The double annular combustion tube shown at B, Fig. 1, was set up horizontally in the 6 in. furnace and a mixture of pentane-air in combining proportions was supplied at 200 cc. per min. The average velocity of gas flow through the annular space was, therefore, 2.7 cm. per sec. and 116 cm. per sec.

through each of the four orifices set at the position of maximum temperature. Velocity ratio remains unchanged on heating. The flow configuration at the position of the communicating orifices is, of course, somewhat speculative but it can be calculated from the width of the outer annulus and orifice diameter that the increased velocity of the reacting mixture flowing through any one of the four orifices at one-quarter of the total rate of supply prevails over a disk 6.7 mm. only in diameter. Thus it may be assumed that the otherwise nearly laminar flow became of a turbulent nature over a relatively small area.

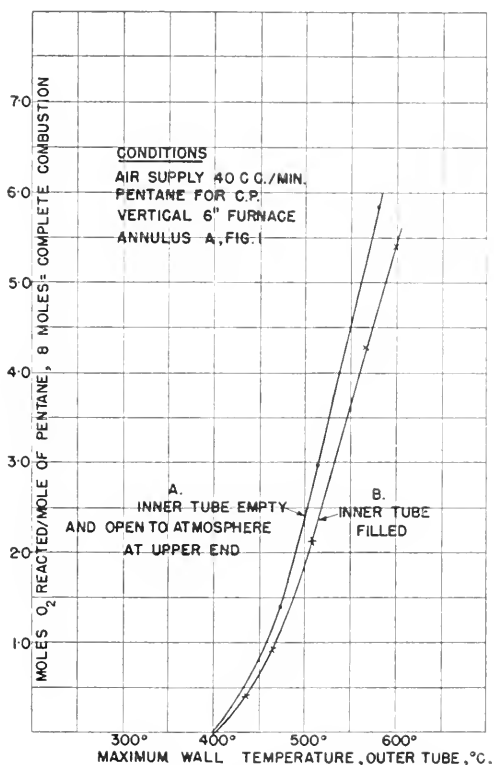


FIG. 3. Change of reaction rate due to small change of temperature difference between walls of Annulus A, Fig. 1.

Reaction rate at temperatures rising to over 600° C. are given by Graph A of Fig. 4 and, for convenient comparison, similar rates obtained for the single annulus in which laminar flow was disturbed by temperature difference only are given by Graph B of the figure, together with rates of formation of carbon oxides.

Referring to Fig. 4, Graph A, it will be noted that, (a) reaction begins at about 125° C. lower than in the single annulus in which flow configuration is nearly laminar, (b) the form of Graph A over the temperature range 400° to 500° C., within which no measurable reaction occurred in the single annulus,

is significant of the formation of partial oxidation products as indicated by the aldehyde hump, (c) at temperatures above the 530°C . at which reaction began in the single annulus, oxidation was mainly to the final products, carbon dioxide and steam; at 575°C . the rate was 630% the greater in the double annulus and at 600°C ., the greater by 560%.

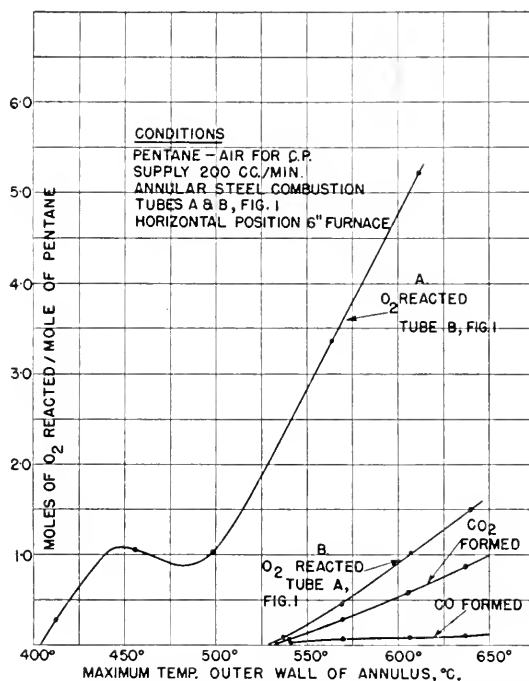


FIG. 4. Effect of local high mixture velocity on reaction in annulus.
Graph A. Mixture passing through orifices, double annulus.
Graph B. Mixture passing straight through single annulus.

Section III

FLOW CONFIGURATION DUE TO HEAT CONVECTION IN UNPACKED COMBUSTION SPACES AND RELATED REACTION VELOCITIES

A useful purpose will be served by discussing the probable flow configuration due to convection currents in an unpacked combustion tube set up vertically in an electric furnace as shown by Fig. 5. When the tube is heated in the usual manner, maximum temperature is reached by a middle part and there are two temperature gradients with a convection circulation over each. The length of the middle part over which there is no temperature gradient depends on the ratio of tube length within the furnace to tube diameter as well as on the width of the space between the inside wall of the furnace and the tube. The figure illustrates the case of a $1\frac{3}{16}$ in. tube supported in a furnace of 2.0 in. internal diameter and 6.0 in. long. The middle part of the tube, of

uniform temperature, does not exceed 1 in. in length and the ratio $\frac{dl}{dt}$ for the temperature gradients increases as the temperature of the middle part is raised. The lower end of the tube contains cold gas being heated while the upper end contains hot gas being cooled so the value of $\frac{dl}{dt}$ is the greater for the lower of the two temperature gradients. When the temperature of the

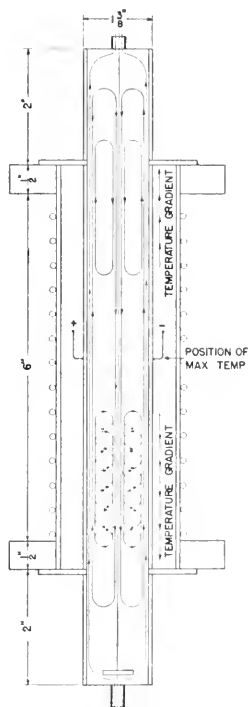


FIG. 5. Possible flow configuration due to convection currents in vertical combustion tube.

middle part of the tube is raised to, say, 600°C . it is reasonable to suppose that cool gas entering at rates of 100 cc. per min. and greater can be raised to that temperature in a tube length of about 3.0 in. solely by repeated contact with the hot walls over the length of the lower temperature gradient. Consequently, the corresponding convection circulation tends to break down into a series of eddies taking the form of rising vortex rings as shown dotted on the diagram. A similar effect would be expected in the upper convection circulation but at the higher maximum temperature required for a suitable value of $\frac{dl}{dt}$. When a 'long' furnace is used and the combustion tube is of relatively small diameter the middle part of the tube attains uniform temperature over a considerable length and convection circulations are set up over the end temperature gradients only, but for tubes of relatively small L/D , as illus-

trated by Fig. 5, the descending stream extends throughout the heated length of the tube. The influence of individual variables on the pattern of the flow configuration would be difficult to determine but assuming that the broad outline is as illustrated by Fig. 5, changes can be effected in various ways and the corresponding reaction velocities measured. This section will be completed by describing a number of related experiments.

Effect of Convection Circulation on the Oxidation of Stainless Steel

A stainless steel (18-8, chromium-nickel) combustion tube $1\frac{1}{4}$ in. internal diameter, set up vertically in a 6 in. furnace was used in earlier experiments to demonstrate the explosion of gaseous combustible mixtures by nuclear drops of water (1). The interior wall of the tube was inspected after hydrogen mixed with air in various concentrations had been passed through it. The rate of supply of the mixture was 200 cc. per min. and maximum wall temperatures varied from 620° to 740° C. The bands of brilliant color seen on the wall were so striking that the tube was split and photographed by infrared light. The photograph is reproduced, Fig. 6. The reddish browns appear as whites and the upper band is overemphasized by glare. It will be noted that oxidation of the steel occurred in the upper and lower parts of the tube. The middle part, at maximum temperature, was coated with blue 'heat scale' and some red that could be seen only by viewing the surface obliquely. Many attempts were made to obtain a greater degree of oxidation of the surface at the middle and hottest position, by changes of hydrogen concentration, but without success. It was supposed at the time of the experiments that the direction of motion of the reacting mixture in the tube was always parallel to the longitudinal axis and, on that assumption, the reason for the formation of oxidation bands *both* top and bottom, *and not at the position of maximum temperature*, remained a mystery. The solution of the 'mystery' is obtained, of course, by abandoning the idea of linear flow, assuming that flow configuration is somewhat as illustrated by Fig. 5 and considering that oxidation of appreciable velocity occurs only at wall surfaces subjected to the scouring action of the eddies accompanying convection circulations.

Direction of Gas Flow and Reaction Velocity

The flow configuration due to convection currents in a combustion tube of relatively large diameter would be expected to differ as between the horizontal and vertical positions and be modified by the direction of gas flow when the tube is in other than the horizontal position. Experiments were made accordingly using a Pyrex tube of 1 in. internal diameter and arranging the gas flow to be vertically upwards or downwards or horizontal. The gas was pentane-air in combining proportions, always passed into the tube at 200 cc. per min. The reaction velocities for the three directions of gas flow are given

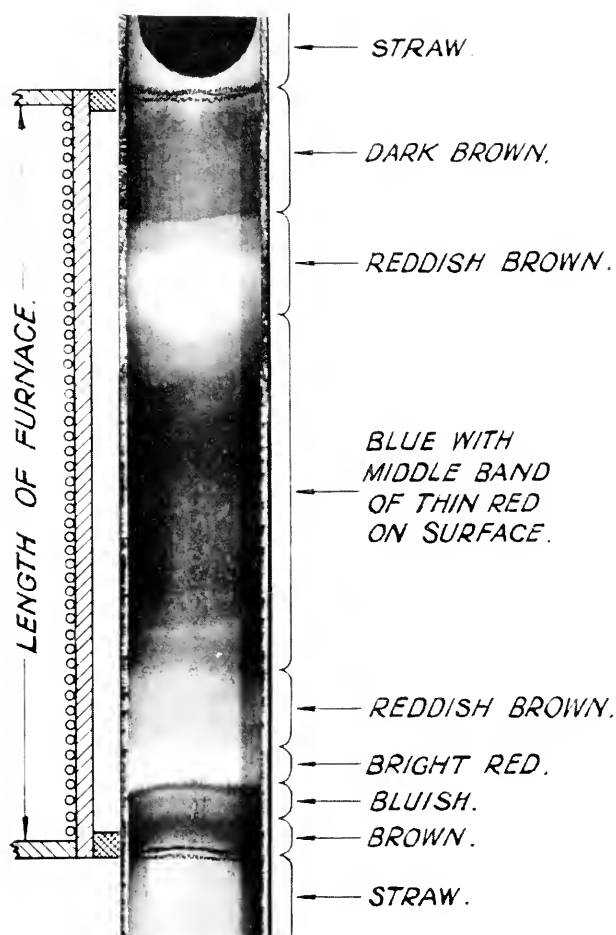


FIG. 6. Effect of flow configuration on the oxidation of a stainless steel tube.

by the graphs of Fig. 7. It will be noted that the smallest reaction rate and the lowest explosion temperature were obtained when the gaseous mixture was forced to flow vertically downward. The reaction rate at the temperature of the aldehyde hump increased by 34% on changing the flow from downwards to horizontal and the rate at 550° C. increased by 75% on changing the flow from downwards to upwards.

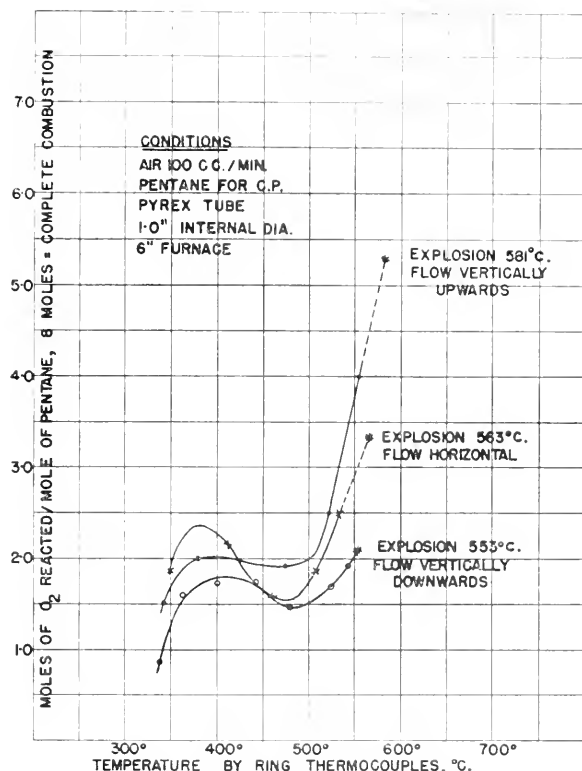


FIG. 7. Effect of direction of mixture flow on reaction rates in Pyrex tube of small L/D .

Effect on Reaction Velocity of Changing Entrance Flow Conditions

The usual method of admitting a combustible gaseous mixture to the cool entrance end of a conventional combustion tube is by a small tube projecting through a cork or rubber stopper as shown at B, Fig. 8. An alternative, generally used in the Cambridge experiments, was the distributor inlet shown at A, Fig. 8. Reaction rates were determined for the two types of inlet, pentane-air in combining proportions being admitted in both cases at 300 cc. per min. The internal diameter of the tube inlet was 6 mm. The velocity of the entering stream was, therefore, 17.7 cm. per sec. as compared with 0.85 cm. per sec. average velocity through the larger tube, and the small stream of relatively high velocity, on reaching the lower convection circulation,

would be opposite in direction to the descending central stream. On the other hand, gas admitted through the distributor inlet enters at the periphery of the combustion tube and rises along the heated walls, the direction of motion coinciding with that of the *ascending* stream of the lower convection

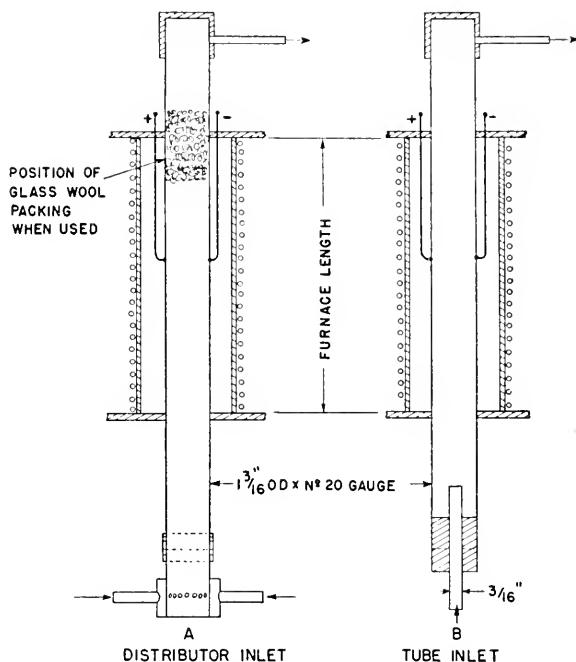


FIG. 8. Mild steel combustion tube with two varieties of gaseous mixture inlet.

circulation. Reaction velocities determined in the two conditions are given by the graphs of Fig. 9 for the temperature range of the aldehyde hump and it will be noted that the rate of oxygen reacted at 450° C., when using the tube

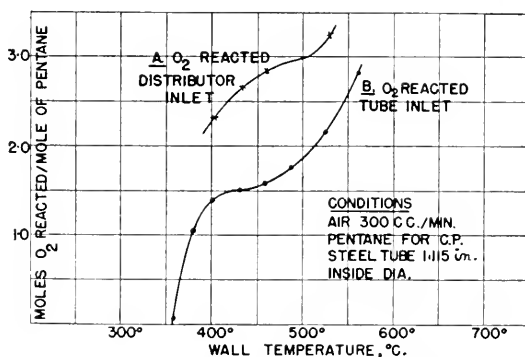


FIG. 9. Effect on reaction rates of change in lower convection circulation due to change of inlet conditions.

inlet, was 1.55 moles as compared with 2.75 moles when the distributor inlet was used. That is, the change in flow configuration due to the use of the distributor inlet accounts for nearly 80% increase in reaction velocity at the temperature mentioned.

Effect on Reaction Velocity of Restricting Upper Convection Circulation

The upper convection circulation in a vertical combustion tube can be restricted to some degree by a plug of loosely packed glass wool, as shown at A, Fig. 8. Reaction rates with and without the packing are given by the graphs of Fig. 10. The distributor inlet was used for both experiments and a

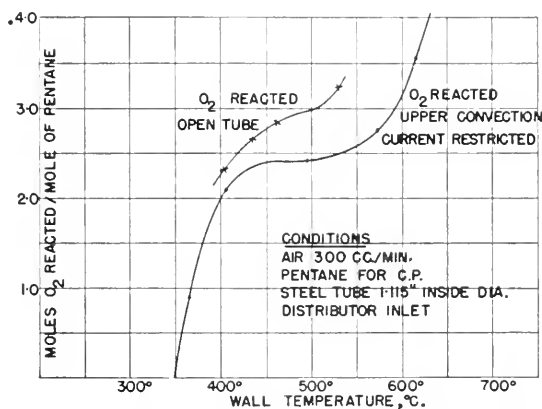


FIG. 10. *Effect on reaction rates of damping upper convection circulation.*

pentane-air mixture in combining proportions admitted at 300 cc. per min. It will be seen by reference to the figure that reaction rate decreased from 3.0 to 2.4 moles of oxygen on restricting the upper convection circulation. The upper circulation is, however, created by the lesser temperature gradient as mentioned earlier and receives partially reacted mixture. Thus, as oxidation of the pentane to aldehyde requires one only of the eight moles of oxygen available, it is probable that reaction accordingly was completed at the position of the lower circulation. The lower reaction velocity at the temperatures of the experiments would, therefore, be expected at the position of the upper convection circulation and change of flow configuration in it would produce less change in the measured over-all reaction rate than if a similar change were made in the lower circulation.

Effect on Reaction Velocity of Changing Flow Configuration in a Single Convection Circulation

The experiments described in preceding paragraphs of this section were made in conditions providing an upper and a lower convection circulation in vertical combustion tubes and 'over-all' reaction velocity only could be determined. The results given below were obtained when using a combustion tube arranged to provide a single circulation extending over the temperature gradient from the middle and hottest part of a vertical combustion tube to the upper end.

The design of the combustion tubes is shown diagrammatically at A and B, Fig. 11. The cool gas of relatively high density admitted at the top of Design A with a velocity of approximately 16 cm. per sec. cannot escape through the outlet without setting up a convection circulation as shown by the diagram.

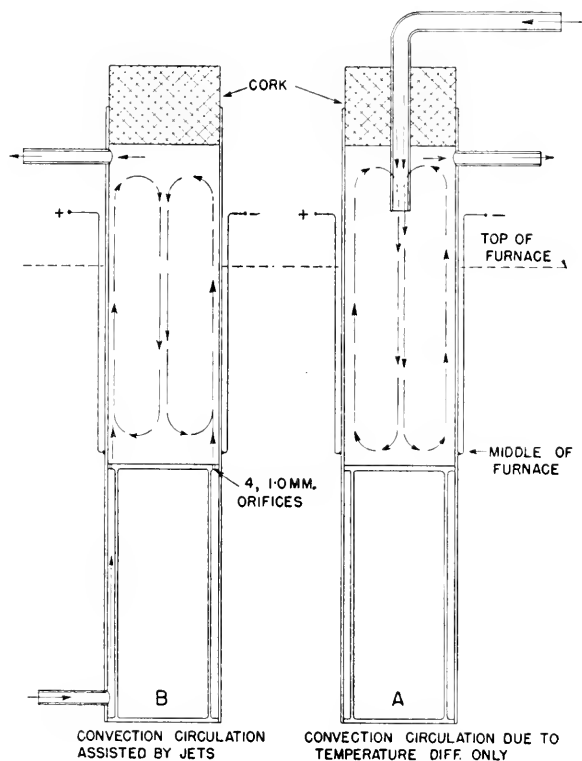


FIG. 11. *Steel reaction chambers in upper half of furnace.*
A. With mixture admitted at relatively low velocity.
B. With mixture admitted by jets assisting convection.

The gas is admitted to Design B at the bottom end and rises through a narrow annulus, in which oxidation is slight, to reach the upper and open space through four 1.0 mm. orifices. The jets issue from the orifices in a position to increase the velocity of the convection circulation already existing by virtue of the temperature gradient but do not impinge on the heated surface of the tube. The odd rate of mixture supply of 167 cc. per min. has no significance.

Reaction velocities determined for the A and B arrangements for pentane-air in combining proportions are given graphically by Fig. 12. It will be seen by reference to Graph A that when flow configuration depended on convection only, the mixture exploded at 600° C. and rate of oxygen reacted never

exceeded 25% of that available. When, however, convection circulation was assisted by the jets, Graph B, reaction was at an extremely high rate but explosion did not occur although the temperature was raised to 660° C. and nearly 95% of the available oxygen reacted accordingly.

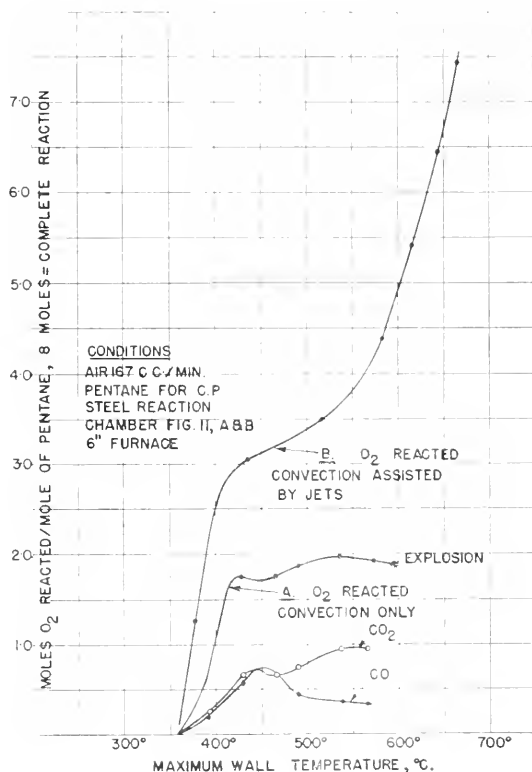


FIG. 12. Effect of change in convection circulation on reaction rates.
Graph A. Reaction rate convection only.
Graph B. Reaction rates with jet assisted convection.

Rates of formation of carbon oxides during the pentane oxidation in Design B are given by Graphs B and C of Fig. 13. It will be noted that carbon monoxide formation reached a distinct maximum at 400° C., which has been found to be the temperature of the maximum rate of aldehyde formation. At temperatures of 450° C. and higher, rate of carbon monoxide formation was just measurable, reaction being substantially to the final products, carbon dioxide and steam. The small hump on the carbon monoxide graph at 650° C. might be attributed to error in measurement but it was obtained on several occasions and is believed to be genuine and possibly due to decomposition products that might be present in small proportion in spite of the high rate of oxidation.

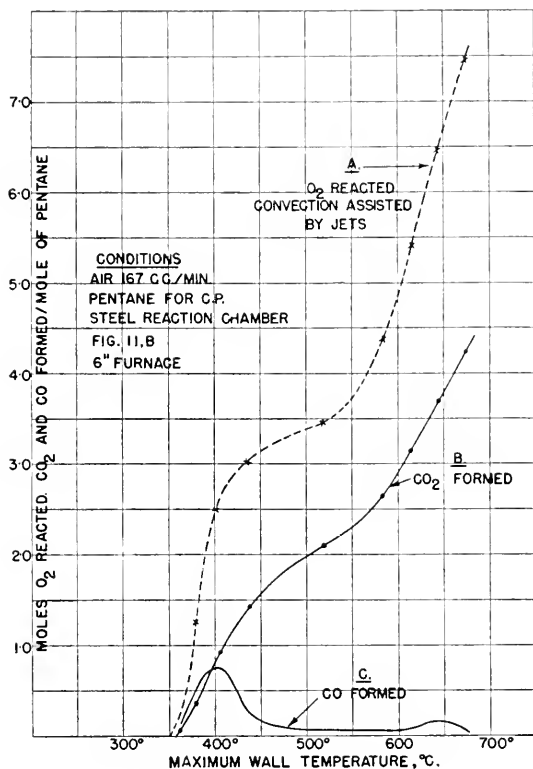


FIG. 13. Carbon dioxide and carbon monoxide formation in reaction with jet assisted convection circulation.

Section IV

REACTION VELOCITY AS AFFECTED BY THE FLOW CONFIGURATION IN REACTION CHAMBER No. 10

Pentane could be oxidized in Reaction Chamber No. 10 (2) at high velocity and the temperature raised, without the occurrence of explosion, until the reaction of oxygen was complete. The flow configuration within the chamber is, therefore, of interest and is indicated by the diagram, Fig. 14, drawn on an enlarged scale. The diameter of the chamber was 1.2 cm., the length 2.2 cm., and the material Jena Supramax glass. The reacting mixture entering through an orifice at the bottom of the chamber forms a streamline jet that impinges on the top surface of the chamber in suitable conditions of pressure and orifice diameter. The laminar flow in the jet is broken on the surface, the reacting mixture fans out and in order to reach the outlet at the bottom periphery of the chamber must move downward along the wall setting up a circulation as shown by the diagram. Eddies or vortex rings probably form between the ascending and descending streams but are not shown by the diagram because the exact flow configuration is speculative. It is important, however, to realize that the velocity of the ascending streamline

jet is greater than that of the stream of gas descending along the wall, in proportion to the respective path areas. The area of cross section of the path of the jet from a 1.0 mm. diameter orifice is 0.0078 cm^2 and that of the return path down the wall, assuming a layer 2.0 mm. thick, is 0.63 cm^2 . Therefore, if gas were supplied at the rate of 100 cc. per min. to the unheated chamber, the

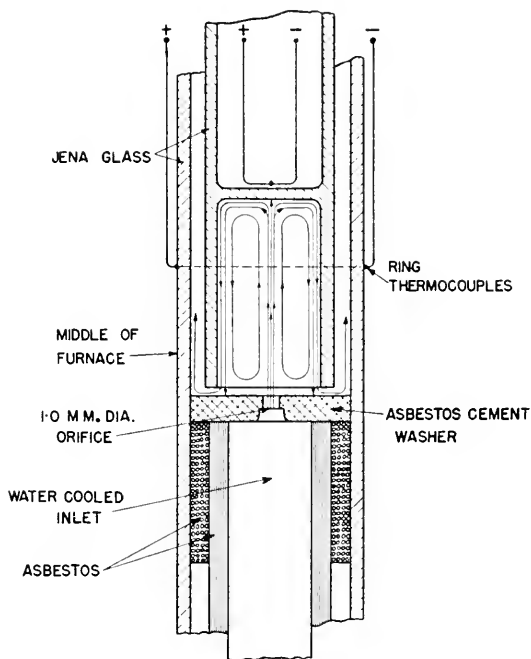


FIG. 14. Diagram of reaction chamber No. 10.

velocity of the jet would be 217 cm. per sec. and that of the descending stream 2.6 cm. per sec. and still less if the stream were thicker than 2.0 mm. The conclusion is that gas flowing through the chamber has a scouring effect on a small circular area of surface of which the position of impact of the jet is the center. The considerations advanced and the experiments described in Sections II and III indicate that reaction to partial products proceeds at an appreciable rate only over the small area mentioned, the remainder of the surface of the chamber being of little practical importance. Experiments supporting this view will now be described.

Effect on Reaction Rate of Changing the Velocity of the Jet While Maintaining a Constant Rate of Gas Supply

Pentane-air in combining proportions was supplied at 50 cc. per min., orifice diameters of 1.0 mm. and 0.5 mm. being used. The velocity of the jet from the larger orifice would then be 108 cm. per sec. and that from the smaller one 432 cm. per sec. if the coefficient of discharge were unity. It was verified by separate experiments, using smoke to make the air flow visible, that the jets

retained a streamline form over the distance from the orifices to the position of impact on the top of the reaction chamber. The velocity of the stream of gas descending along the wall would be unchanged and the sole difference in flow configuration would occur in the small circular area of which the position of impact of the jet is the center. Rates of reaction are shown by the graphs of Fig. 15, and it will be seen that on changing from the larger to the smaller

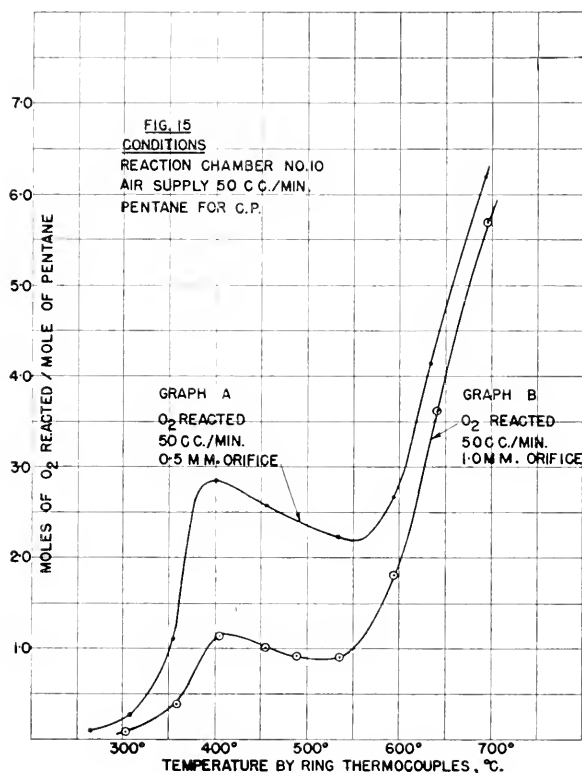


FIG. 15. Effect of jet velocity, reaction chamber No. 10, with constant rate of mixture supply.

orifice, reaction velocity increased over the whole temperature range of the experiment. The increase was greatest at the temperature of the formation of partial oxidation products at the maximum rate and was then nearly 150%. It is to be remembered that rate of aldehyde formation was limited because the reacting mixture contained one mole only of pentane to eight moles of oxygen and therefore all of the pentane could be oxidized to aldehyde by the reaction of one-eighth of the available oxygen.

Effect on Reaction Velocity of Increasing the Proportion of Pentane in the Mixture with Air

The graphs of Fig. 16 show reaction velocities for pentane-air supplied to reaction chamber No. 10 through a 1.0 mm. orifice. Graph A gives rates of oxygen reacted when the mixture contained two moles of pentane to eight

moles of oxygen and Graph B gives rates of oxygen reacted when the mixture contained one mole of pentane to eight of oxygen. The experiments were made in similar conditions of flow configuration and of all other respects and show, as would be expected from considerations already discussed, that the

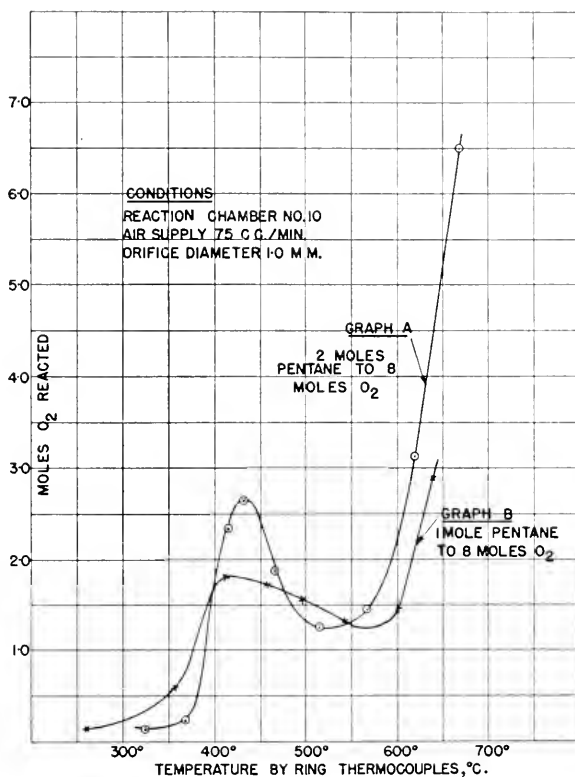


FIG. 16. Effect of increasing pentane concentration in mixture with air, reaction chamber No. 10.

removal of partial oxidation products from a relatively small area of active surface by the scouring action of the jet allows access of unreacted mixture and the formation of such products at a greatly increased rate if the composition of the reacting mixture permits. Thus, the aldehyde hump of Graph A is exceptionally pronounced and maximum rate of reaction at the corresponding temperature is 70% greater than for the mixture containing half as much pentane and oxidized in the same conditions of flow configuration.

Effect on Degree of Oxidation of Time of Exposure and Flow Configuration

When a reacting mixture is supplied to reaction chamber No. 10, having a volume of 2.5 cc., at the rate of 50 cc. per min., the time of exposure to the oxidizing conditions, as usually calculated, is 3.0 sec. and the flow configuration is fixed by the diameter of the admission orifice. The rate of supply being increased to 150 cc. per min., the time of exposure is reduced to 1.0 sec.

but if the diameter of the orifice remain unchanged, flow configuration is altered by the velocity of the jet having increased by 300% with a corresponding increase in the scouring effect on the surface on which the jet impinges. The results of experiments made accordingly are given by the graphs of Fig. 17 and it will be seen that over the low temperature range a maximum of

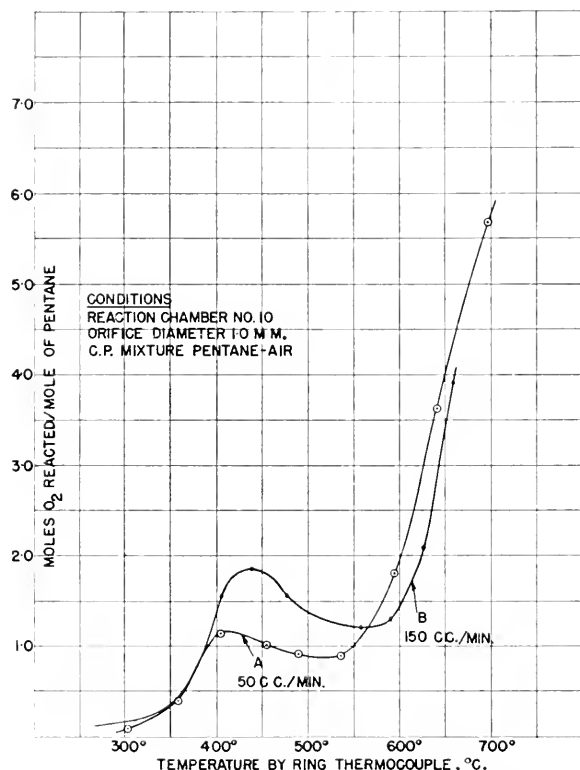


FIG. 17. Effect of threefold increase in rate of mixture supply, reaction chamber No. 10.

1.8 moles of oxygen was reacted in the 1.0 sec. exposure time and 1.2 moles only in the 3.0 sec. time. Even over the higher range of temperature for which reaction is mainly to final products the increase of 300% in exposure time accounted for a relatively small decrease in moles of oxygen reacted.

Section V

CONCLUSIONS

The experiments described in preceding sections were concerned with the oxidation of pentane in air but the results are probably of more general application. It is suggested for discussion and for further experimental work—

(a) That the reduction in reaction velocity obtained on packing an open combustion space is not due to an increase of surface but to the consequent change in the flow configuration of the reacting mixture.

(b) That the oxidation of pentane is a heterogeneous reaction, velocity depending on flow configuration and the nature of the surface of the reaction space. The graphs of Fig. 18 are given in support of the suggestion.

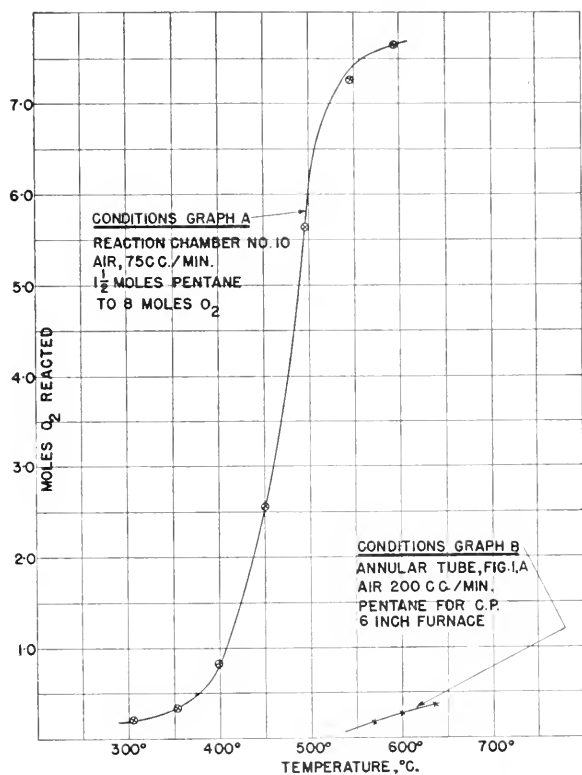


FIG. 18. Nearly complete or nearly zero reaction depending on flow configuration and nature of surfaces.

Graph A, showing a remarkable rate of oxidation with completion of the reaction without explosion at 600° C., was obtained for an oxidation in reaction chamber No. 10 of pentane containing iron carbonyl in the concentration of 0.67%. The mixture with air contained 50% more pentane than required for combining proportions. The reacting mixture was, as shown by the experiments of Part I, brought, by the flow configuration in the reaction chamber, into intimate contact with a small surface area of iron maintained in an oxidizing atmosphere by continuous deposition from the carbonyl. In spite of the extremely high reaction velocity, oxidation was, at all temperatures, straight through to carbon dioxide and steam, no more than a trace of aldehyde or carbon monoxide being found in the products.

Graph B was obtained in conditions of nearly laminar flow combined with an inactive surface for a mixture of pentane with air in combining proportions. The steel annular combustion tube A, Fig. 1, was used for the experiment and the surface was rendered inactive in respect of the carbon dioxide steam

reaction by a catalyst poison, ethyl mercaptan, added to the pentane in the concentration of 2%. It will be seen by reference to the graphs that reaction *began* at about the temperature of completion in the conditions used to obtain Graph A, and increased relatively slowly with further increase of temperature.

Acknowledgments

The experimental work described in this paper is part only of that carried out in the Colloid Science Laboratory, Cambridge, with the co-operation of Prof. E. K. Rideal and Dr. F. H. Garner.

The laborious and accurate gas analyses work was undertaken by Mr. R. R. Davidson, Emmanuel College, Cambridge, to whom credit is given for improvements in methods of using the Ambler apparatus.

Dr. E. W. R. Steacie and Dr. L. Marion, both of the National Research Council, have assisted by reading the text and advising accordingly.

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THE OXIDATION, IGNITION AND DETONATION OF FUEL VAPORS AND GASES

III. THE CAUSE OF THE EFFECT OF METALLIC DOPE TO DELAY DETONATION¹

BY R. O. KING²

Abstract

The antiknock effect of metallic dope is attributed to the catalytic action of the surface, maintained in an oxidizing atmosphere by continuous deposition thereon of the metal of the dope, to oxidize the fuel in part to steam and carbon dioxide, the consequent dilution of the end gas causing a reduction of inflammability sufficient to prevent completion of combustion in other than the normal manner. Experiments indicate that temperatures required for the necessary catalytic activity are attained during the period of flame travel; not prior to ignition. In support of the theory experimental evidence is given showing that, (a) steam is especially effective to reduce inflammability, (b) doped pentane or hexane oxidizes without ignition to steam and carbon dioxide only in reaction chamber No. 10, described in Part I, at any temperature of reaction, (c) the carbon dioxide-steam reaction is inhibited by a sulphur catalyst poison and the similar action in the engine destroys the antiknock effect of the dope. It is shown further by experiments with and without additions of a catalyst poison to *undoped* engine fuel that, in conditions leading to high surface temperatures in the combustion space, a carbon dioxide-steam reaction having a considerable antiknock effect is obtained. The engine experiments with catalyst poisons are completed by obtaining conditions in which tetraethyl lead becomes a pro-knock. It is recognized that the catalyst theory depends fundamentally on the oxidation of hydrocarbon fuel being a heterogeneous reaction as indicated by the experiments described in Part II, and some further evidence in support of the view, obtained by using catalyst poisons, is given in this Part.

Introduction

The discovery by Midgley and Boyd of the remarkable effect of tetraethyl lead present in extremely small concentration in engine fuel, to delay the onset of detonation as the compression ratio is raised, was followed by a spate of explanatory theories, the number extending ultimately to more than a dozen. Those proposed prior to 1926 and reviewed by Clark and Thee (5) did not involve a departure from accepted belief concerning the mechanism of the oxidation of the paraffin hydrocarbons present in large proportion in normal engine fuel and mainly responsible for the occurrence of detonation.

Such a departure was made in the Callendar nuclear drop-peroxide theory (3, 4) submitted to the Aeronautical Research Committee, December, 1926, in that oxidation was taken to begin with the formation of an organic peroxide instead of in hydroxyl compound as required by the generally accepted, Armstrong-Bone hydroxylation theory. Support was afforded the peroxide theory by the work of Moureu, Dufraisse, and Chaux who followed Callendar in associating peroxides with fuel detonation (15).

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Egerton and Gates (6), in a review of the theories of antiknock action, agreed that peroxides, acting as autocatalysts, are formed in the early stage of combustion and suggested that metallic antiknocks form comparatively stable peroxides which react with and destroy the fuel peroxides which are then regenerated. The suggestion led Egerton (7, pp. 2911–2926) to the formulation of a chain reaction theory in which peroxide is an essential link, the development of the reaction to cause knocking being interrupted on the destruction of the peroxide by the metal of the dope, which is oxidized in the process. Finally, Beatty and Edgar (2, pp. 2927–2936) in a comprehensive review of the theory of knock in internal combustion engines conclude that “antiknock agents act as inhibitors for the slow oxidation reactions in the end gas. Their effect is to break short the reaction chains and so prevent the chain development from reaching that critical point at which its multiplication begins”.

Theories that antiknocks act by destroying organic peroxides or by breaking reaction chains in an homogeneous fuel–air mixture are not accepted but discussion can be reserved. The reviews mentioned do, however, deal with two matters related to experimental work described in Parts I (8) and II (9) and later in this Part.

Beatty and Edgar mention particularly the difficulty of relating oxidation as it occurs in laboratory experiments to the similar effect in the end gas of an engine. Thus it is stated that laboratory oxidations cannot be carried to temperatures higher than 500° C. because of the incidence of ignition or explosion, and that time of reaction is sometimes 1000-fold greater than in an engine. The statements were, of course, made before the development of reaction chamber No. 10, described in Part I (8) in which it is possible to carry laboratory oxidations of hydrocarbons commonly used as engine fuel to whatever temperature is required for completion, 700° C. or over, without ignition and in reaction times of a second or less.

The positive catalyst theory, which assumes that antiknocks accelerate oxidation *prior to ignition* in the engine and accordingly weaken the mixture to an extent sufficient to prevent detonation, is mentioned by Egerton with the comment that the antiknocks retard oxidation and consequently the theory is contrary to fact. Beatty and Edgar also mention the theory and dismiss it on sounder grounds by observing, in effect, that promotion of the oxidation of the fuel by antiknocks during the *early stages of combustion* in an engine is not in accordance with experimental facts.

Revised Positive Catalyst Theory

The experiments described in Part I (8) and others to be described in this Part show that the oxidation of paraffin hydrocarbons doped with iron carbonyl, in reaction chamber No. 10, which provides conditions approaching those obtaining in the combustion space of an engine, is a heterogeneous reaction on a surface of iron maintained as such in an oxidizing atmosphere by continuous deposition of metal from the organic compound. The final

products only, namely steam and carbon dioxide, are produced at any temperature of reaction. The reaction does not proceed with high velocity until surface temperature exceeds 500°C . Such high surface temperatures would be found in the combustion space of an engine on the exhaust valves in conditions of maximum power output and momentarily on other surface exposed to radiation from the advancing flame which reaches temperatures of 2500°C . and over, depending on compression ratio and other factors. The end gas in which detonation occurs is heated by compression to temperatures of 650°C . and over, depending on compression ratio, and would be expected to attain even higher temperatures because of turbulence. Temperature and turbulence conditions are, therefore, as required to promote extremely rapid surface oxidation of the doped fuel to final products which could reduce the inflammability of the end gas to such an extent that completion of combustion would be possible solely by normal flame travel. An adequate explanation for the antiknock action of metallic dopes is then obtained without having to determine the cause of detonation.

Section I

EFFECT OF STEAM TO REDUCE INFLAMMABILITY

The effect of steam, nitrogen, and carbon dioxide as diluents on the inflammability of a normal fuel-air mixture used in the E 35 engine was determined by Ricardo (17). The work was extended and the experimental results discussed some time later by Alcock (1). The gases mentioned were added to the fuel-air charge in increasing proportion until inflammability was so reduced that misfiring occurred. It was emphasized that elaborate precautions, including superheating, were required to ensure that steam was added to the engine charge as such, not as part water.

It was found that 8.9% of steam sufficed to reduce inflammability to the extent required to cause misfiring although flame temperature was reduced by 125°C . only. Carbon dioxide was required in the proportion of 19.6% to produce a similar effect although flame temperature was reduced by 400°C . The conclusion was that steam exerted a nonthermal effect to reduce inflammability, the nature being unknown. Whatever the nature of the effect may be, the magnitude is of great importance, and from the data given above it is calculated that, on a weight basis, steam is six times more effective than carbon dioxide, the other product of the complete combustion of hydrocarbons.

Effect of Steam to Reduce the Inflammability of Hydrogen

Hydrogen is especially suitable for experiments to determine the effect on inflammability of steam which is the sole final product of oxidation. It was mentioned, Part I (8), that tetraethyl lead and iron carbonyl had been shown by Mardles to promote the oxidation of hydrogen. The rate of oxidation was not, however, related to inflammability, and the experiment using the carbonyl as the oxidant has been repeated in carefully controlled

conditions and using a conventional flow method. The combustion tube was of silica, 1 in. internal diameter, supported in a vertical 6 in. furnace. Silica was selected because of its relatively inactive surface. The hydrogen and air were from high pressure cylinders and, therefore, nearly dry, but, as a further precaution, the gases were passed over phosphorus pentoxide while en route to the combustion tube. The reacting mixture was supplied at the rate of 200 cc. per min. and contained hydrogen in the concentration of 40% by volume. Iron carbonyl, as vapor, was added to the air stream at the rate of 40 mgm. per hour. Temperatures were taken by means of a thermocouple in a silica sheath placed at the position of maximum temperature on the longitudinal axis of the combustion tube. The hot gases from the combustion tube were passed through a Liebig condenser and then through a U-tube

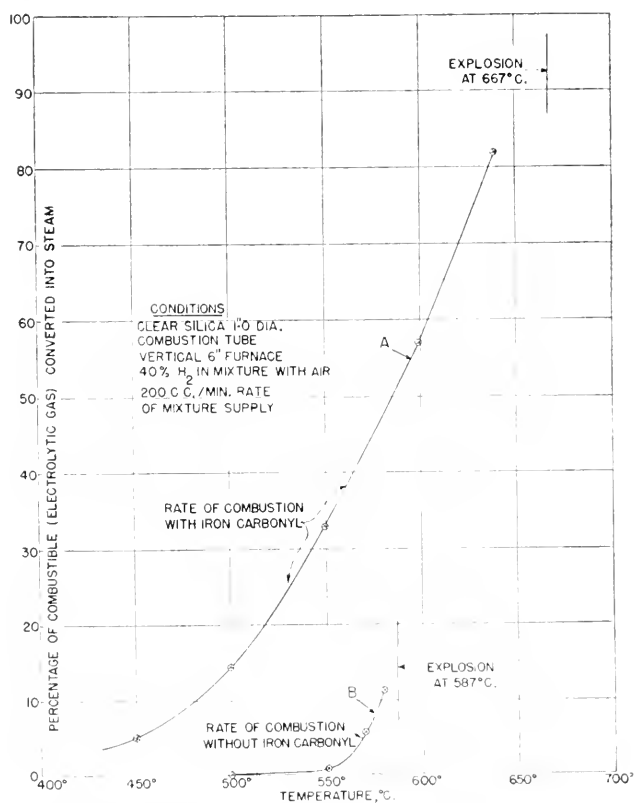


FIG. 1. Graphs showing the effect of steam from a heterogeneous reaction to reduce inflammability and thereby raise explosion temperature.

containing calcium chloride. Rates of oxidation were measured by weighing the water of combustion at suitable time intervals. When iron carbonyl was added to the reacting mixture, iron oxide was deposited on the tube at the positions of the upper and lower convection circulation, see Fig. 5, Part I (8), and in view of the fact that the mixture contained both oxidizing and reducing

gases, care was taken that the equilibrium oxide had formed prior to measuring rate of combustion. Equilibrium was taken as having been established at a particular temperature when water of combustion was obtained at a constant rate.

Graph *A* of Fig. 1 gives rates of steam formation when the hydrogen-air mixture contained the vapor of iron carbonyl, and Graph *B*, rates of steam formation when the mixture without the vapor was passed through the tube in clean condition. It will be noted that with iron carbonyl present combustion of electrolytic gas occurred at the easily measurable rate of 5%, at 450° C., whereas the rate was about 1% only at 550° C., in the absence of the carbonyl and 33-fold greater when it was present. The mixture containing iron carbonyl exploded at 667° C. and at 587° C., in the absence of the carbonyl.

Concluding Comments

The experiments by Ricardo and Alcock show the effect of steam from an outside source to reduce the inflammability of the reacting mixture in an engine. Those just described show a similar effect obtained by steam produced by the reaction itself.

Section II

THE OXIDATION OF PENTANE IN REACTION CHAMBER NO. 10, AS AFFECTED BY IRON CARBONYL

The reaction chamber was described in Part I (8), and experiments on the effect of flow configuration described in Part II (9) indicated that oxidation in the chamber is a heterogeneous reaction so far as doped pentane is concerned and probably of a similar character in respect of pentane alone. Experiments described in this section were made to confirm the earlier results and to determine the effect on rate of oxidation of changing the concentration of iron carbonyl and the effect of a residual surface of iron oxide.

The experimental results shown by the graphs of Figs. 7, 8, 9 and 10 of Part I (8) were obtained immediately after the completion of the reaction chamber. The chamber was then dismantled, cleaned with hydrofluoric acid, washed with steam, and an oxidation of pentane containing iron carbonyl in the concentration of 0.5% repeated. The experimental results are plotted on Graph *B* of Fig. 2, together with those obtained earlier, and it will be noted that the two sets of results fall on a single curve showing a degree of repeatability not generally obtained when using conventional methods.

The increase in rate of reaction obtained on doubling the dope concentration is shown by Graphs *B* and *C* of Fig. 2. A useful comparison can be made at the temperature of 550° C., when about half of the oxygen remained uncombined. The increase was from 4.1 to 5.5 moles of oxygen reacted, that is, 30%. Flow configuration was similar for both experiments and the increase is attributed to some possible increase in the area of the effective catalytic iron surface or to an increase in the density of the catalyst.

Rates of formation of carbon oxides for the smaller concentration of iron carbonyl were given by the graphs of Fig. 8, Part I (8). Exactly similar results were obtained when using the larger concentration and as before reaction was substantially to steam and carbon dioxide whatever the temperature.

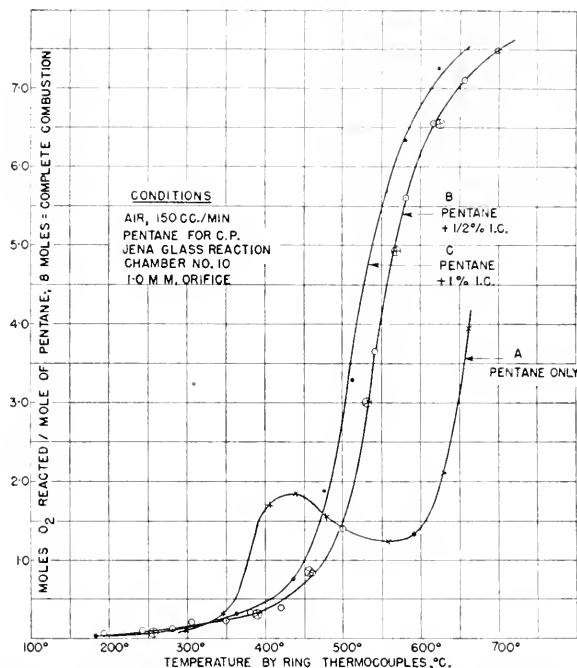


FIG. 2. Graphs showing the increase in velocity of the carbon dioxide-steam reaction due to doubling the iron carbonyl concentration in pentane.

Pentane Oxidation on Residual Oxide Surface

The coating of the surface of the reaction chamber with iron and iron oxides seen after oxidation of pentane doped with iron carbonyl was shown, *B*, Fig. 6 of Part I (8); distribution varies with rate of mixture supply and the concentration of iron carbonyl in the pentane and thickness with time of use of the doped pentane, but the surface becomes completely coated with brick red oxide on continued use of the chamber with undoped mixture. The results of an oxidation of pentane after use of the chamber with pentane containing iron carbonyl in the concentration of 1.0% are given by Graph *C* of Fig. 3. Graph *A* for pentane oxidized in the chamber when clean and Graph *B* for the oxidation of pentane plus 1.0% iron carbonyl are given for case of comparison. The graphs show that when the metal surface was no longer maintained by continuous deposition from the carbonyl, rates of reaction at temperatures above 500°C. are greatly reduced and tend to approach those obtained when the reaction chamber surface is clean glass. Thus at 550°C. rate of reaction fell from 5.2 moles, Graph *B*, to 1.8 moles of oxygen reacted, Graph *C*. At 625°C., oxygen was reacted at the rate of

7.25 moles when using the doped mixture, Graph *B*, but diminished to 5.8 moles for the residual surface, Graph *C*, and further to 4.6 moles after $3\frac{1}{2}$ hr., as shown by the single observation marked with an arrow below Graph *C* of the figure.

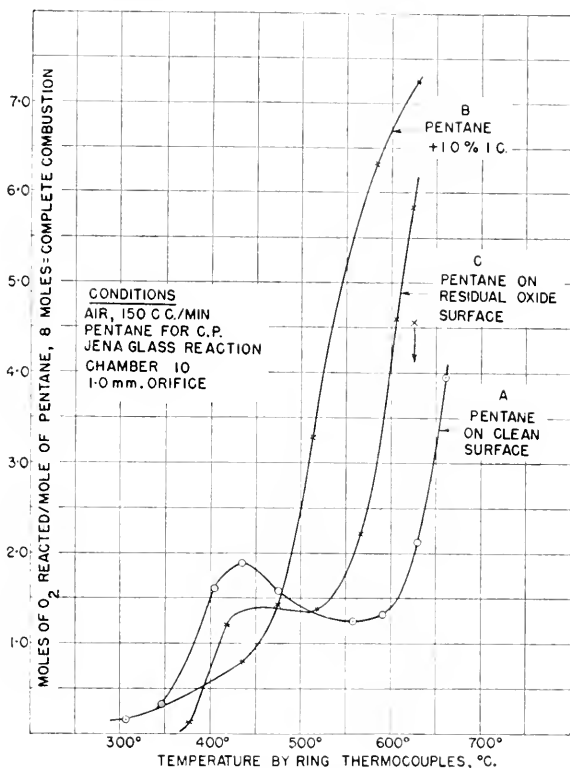


FIG. 3. Graphs showing the effects on the oxidation of pentane of ceasing to maintain the catalytic surface provided by continuous deposition of iron from the carbonyl.

The reappearance of the aldehyde hump, Graph *C* of Fig. 3 when the active metal surface of the reaction chamber surface was converted to oxide is of great interest and supports the view, expressed in Section V of Part II (9), that the oxidation of pentane to partial products, including aldehyde, is a heterogeneous reaction.

Section III

THE OXIDATION OF HEXANE IN REACTION CHAMBER NO. 10, AS AFFECTED BY IRON CARBONYL

Hexane is present in considerable proportion in normal engine fuel and is of relatively low octane number. Experimental results for the effect of metallic antiknocks on the oxidation of the substance, hitherto published, have always been obtained by conventional methods and because of the almost complete oxidizing nature of combustible mixtures with air, reaction could not occur on a surface of metal deposited from the dope, except at very

low temperatures. The consequent effect of the dope to inhibit the oxidation of hexane and higher paraffins in the same circumstances is the experimental basis of current theory attributing the antiknock action to an antioxidant property. It became of special interest, therefore, to determine if the oxidation of hexane in reaction chamber No. 10 at high temperatures would be promoted on the addition of metallic dope and if reaction would be to final products as for pentane oxidation.

Oxidations in Reaction Chamber No. 10

The experimental conditions were as described for oxidations of pentane. The 'hexane', supplied by the Anglo-American Oil Company, was procured from the fractional distillation of nearly aromatic-free petroleum spirit. The density was 0.6965, and distillation range 62° to 85° C. for a 95% fraction.

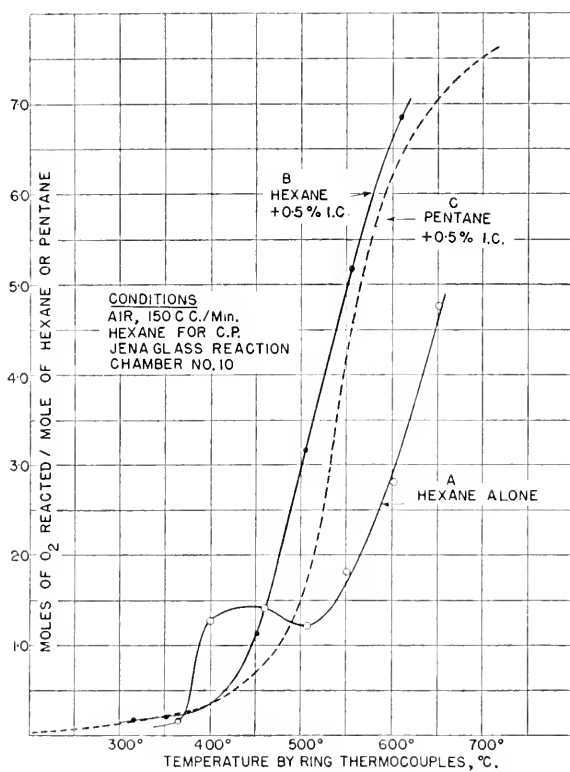


FIG. 4. Graphs showing the effect of iron carbonyl to promote the oxidation of hexane at high temperatures as compared with the similar effect for pentane.

Experimental results are given by the graphs of Fig. 4: Graph A is for hexane alone in the reaction chamber in clean condition; Graph B is for hexane plus iron carbonyl in the concentration of 0.5%. The combining proportions mixtures used for the experiments were made up on the assumption that the hexane was normal and that $9\frac{1}{2}$ moles of oxygen would be required accordingly

for the complete oxidation of one mole of the paraffin. It will be noted that the characteristics of hexane oxidation are similar to those determined for the oxidation of pentane. Graph *C* of the figure, for the oxidation of doped pentane, is reproduced from Fig. 2 and appears to show that iron carbonyl possesses the greater oxidation promoting effect in respect of pentane, but, when allowance is made for the specific oxygen consumption, the carbonyl is found to be of equal effect in respect of the two paraffins, as nearly as can be determined without exact knowledge of molecular composition.

The oxidation of doped hexane was, as for doped pentane, substantially to steam and carbon dioxide at any temperature of reaction, as shown by the graphs of Fig. 5.

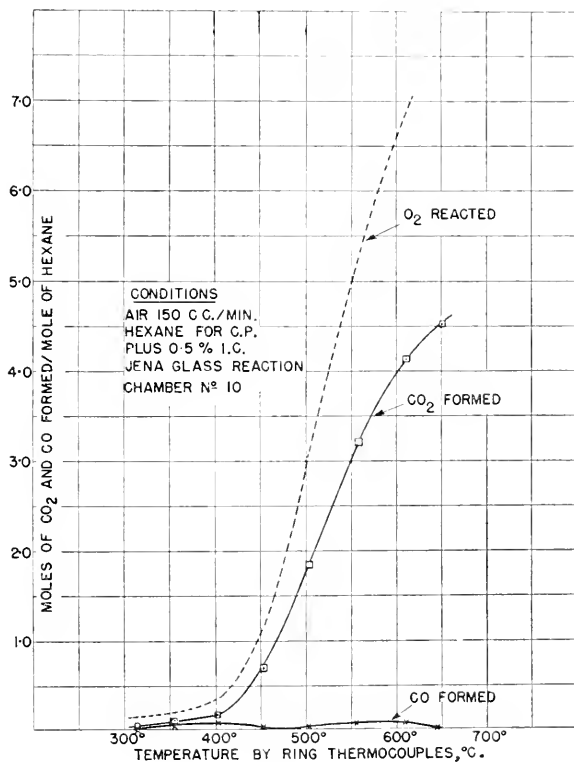


FIG. 5. Graphs showing that the oxidation of hexane containing iron carbonyl is substantially to carbon dioxide and steam at all temperatures of reaction.

Section IV

THE SPECIFIC EFFECT OF ETHYL MERCAPTAN TO INHIBIT THE HETEROGENEOUS REACTION OF PENTANE AND HEXANE TO STEAM AND CARBON DIOXIDE

Having shown that the antiknock, iron carbonyl, suppresses the formation of partial oxidation products, including aldehyde, and promotes the formation of steam and carbon dioxide at all temperatures of reaction, it remains to

determine which of the two effects is responsible for the antiknock property of the carbonyl. The use of a catalyst poison in oxidation and related engine experiments makes it possible to distinguish between the effects mentioned.

Ethyl Mercaptan and Hydrogen Sulphide

The one hydrogen atom of the mercaptan and the two of the sulphide are replaceable by metal. Either substance converts a contact surface of iron to one of iron sulphide and is without effect on a surface of iron oxide. Both substances were known from earlier experiments to destroy the antiknock effect of the metallic dopes. The mercaptan, rather than hydrogen sulphide, was used for laboratory experiments to avoid the complications involved in the supply and measurement of the sulphide at the small rates required. The concentration of 2.5% by weight of the mercaptan in the pentane and hexane is without significance except that in engine experiments it was sufficient to destroy the antiknock effect of 2 cc. per gal.* of tetraethyl lead in an engine fuel.

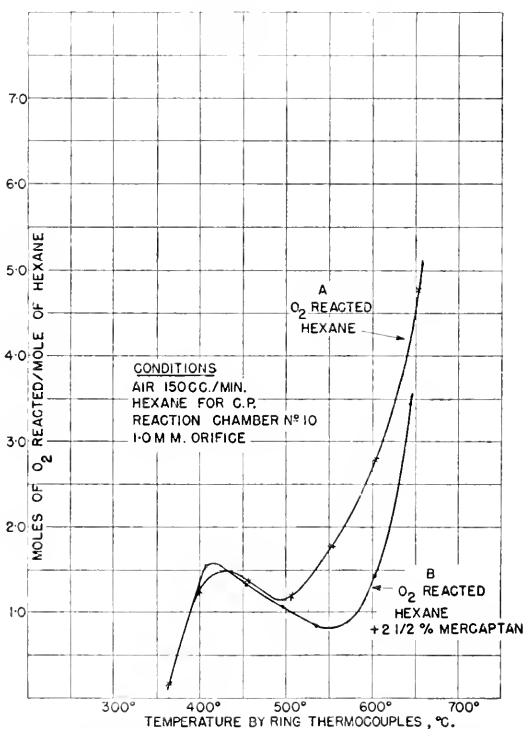


FIG. 6. Graphs showing that ethyl mercaptan, a catalyst poison, does not affect the aldehyde reaction in a glass reaction chamber (No. 10).

Effect of Ethyl Mercaptan on the Oxidation of Hexane in Reaction Chamber No. 10

The experimental results are given by the graphs of Figs. 6, 7, and 8. It is of special significance, as shown by the graphs of Fig. 6 for oxygen reacted,

* References throughout this paper are to the imperial gallon.

that the mercaptan had no measurable effect on reaction velocities at temperatures below about $480^{\circ}\text{C}.$, that is, at the temperatures of the formation of partial products including aldehyde. The inhibitory effect was confined to the carbon dioxide-steam reaction as shown by the graphs of Figs. 7 and 8 for rates of formation of carbon oxides.

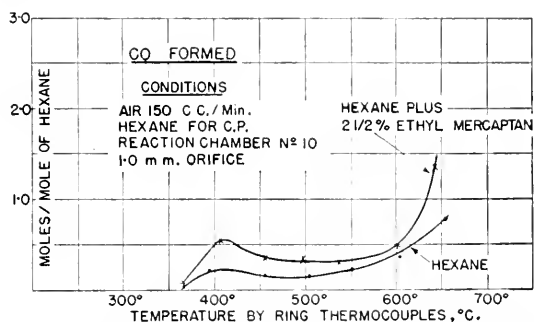


FIG. 7. Graphs showing the effect of ethyl mercaptan on carbon monoxide formation when hexane is oxidized in reaction chamber No. 10.

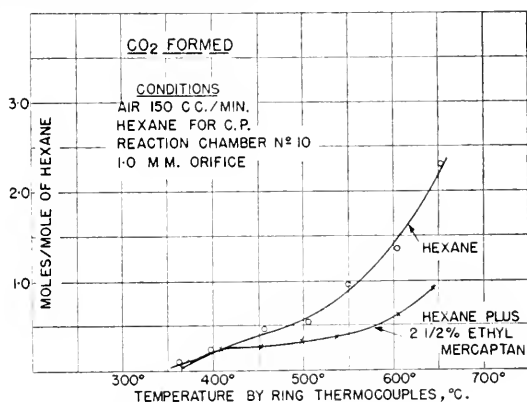


FIG. 8. Graphs showing the effect of ethyl mercaptan on carbon dioxide formation when hexane is oxidized in reaction chamber No. 10.

Effect of Ethyl Mercaptan on the Oxidation of Hexane plus Iron Carbonyl in Reaction Chamber No. 10

The experimental results are given by the graphs of Figs. 9, 10, and 11. At $550^{\circ}\text{C}.$ oxygen was reacted at the rate of 5.0 moles when the pentane contained 0.5% of iron carbonyl, Graph A, Fig. 9. The rate was 1.2 moles only when the doped pentane contained $2\frac{1}{2}\%$ of mercaptan. Carbon dioxide, at the same temperature, was formed at the rate of 1.75 moles without the mercaptan and 0.25 moles with it. Carbon monoxide formation, Fig. 11, was inappreciable in either case. At $600^{\circ}\text{C}.$ oxygen reacted was 6.6 moles without the mercaptan and 0.8 moles with it. There was a corresponding change in rate of carbon dioxide formation, and carbon monoxide formation occurred at an appreciable rate, 0.25 moles.

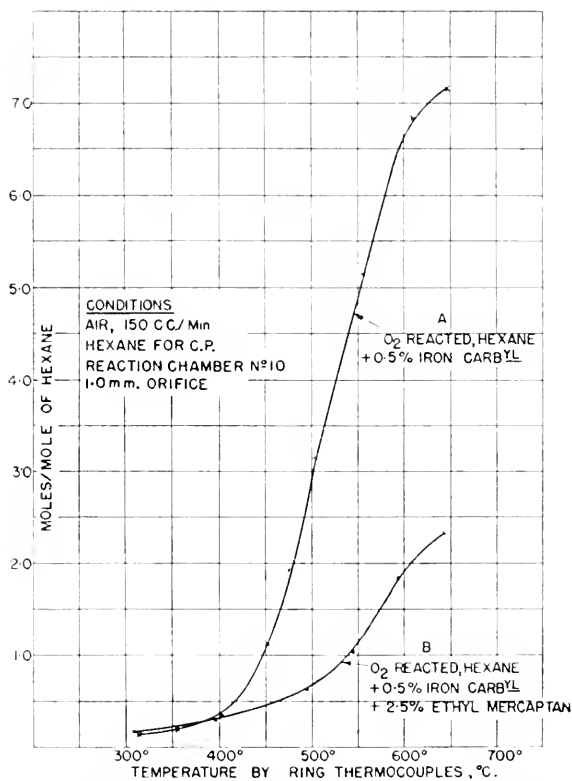


FIG. 9. Graphs showing the inhibiting effect of ethyl mercaptan on the oxidation of hexane doped with iron carbonyl in glass reaction chamber (No. 10).

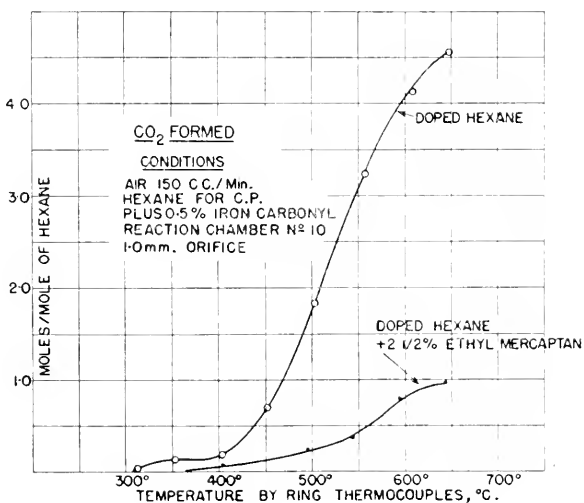


FIG. 10. Graphs showing the effect of ethyl mercaptan on carbon dioxide formation when doped hexane is oxidized in glass reaction chamber (No. 10).

The Effect of Ethyl Mercaptan on the Oxidation of Pentane in Reaction Chamber B, Fig. 11, Part II (9)

The reaction chamber was of mild steel which does not rust uniformly. The surface in contact with the reacting mixture of pentane-air would, therefore, comprise areas of iron oxide which would promote the formation of

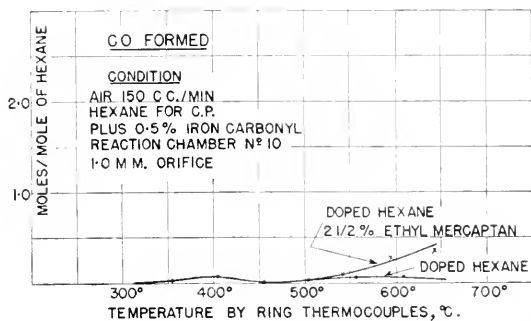


FIG. 11. Graphs showing the effect of ethyl mercaptan on carbon monoxide formation when doped hexane is oxidized in glass reaction chamber (No. 10).

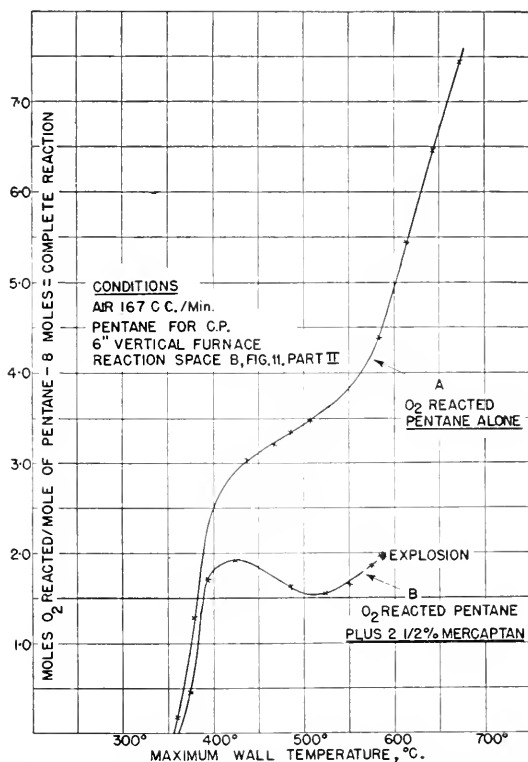


FIG. 12. Graphs showing the effect of ethyl mercaptan on the oxidation of pentane (undoped) in a steel reaction chamber.

partial oxidation products and areas of iron which would promote oxidation to final products, and, as there existed a steep temperature gradient over the length of the chamber, reaction can occur at a range of temperatures even when the maximum is 600°C. or over. The mixed nature of the reaction in the chamber is shown by Graph *A* of Fig. 12, which is characteristic of both the aldehyde and the carbon dioxide-steam reactions. The effect of the mercaptan is shown by Graph *B* of the figure. The carbon dioxide-steam reaction is nearly eliminated, as shown by the graphs of Figs. 13 and 14, leaving the aldehyde, which, in the absence of dilution with steam and carbon dioxide, ignites and explodes when the temperature reaches 590°C.

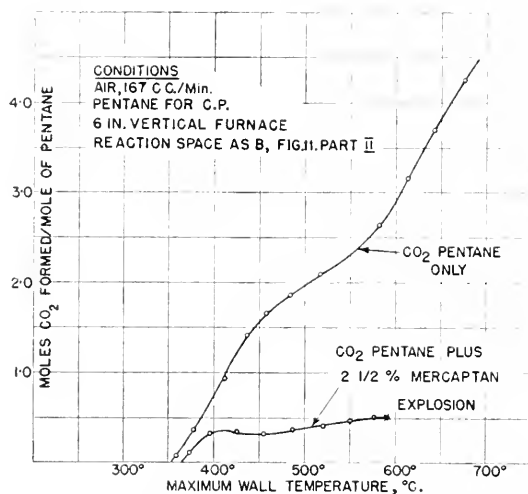


FIG. 13. Graphs showing the effect of ethyl mercaptan on carbon dioxide formation when pentane is oxidized in the steel reaction chamber.

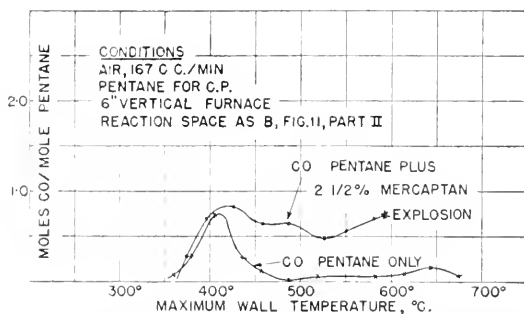


FIG. 14. Graphs showing the effect of ethyl mercaptan on carbon monoxide formation when pentane is oxidized in the steel reaction chamber.

Pentane Oxidation on Surface Remaining after the use of Mercaptan

An oxidation of pentane in the steel reaction space, as above, was carried out after the oxidation of pentane plus the mercaptan. The experimental

results are given by the graphs of Fig. 15 and show a considerable residual effect. Thus, for example, at 550°C ., 3.8 moles of oxygen were reacted when the reaction chamber was first used. The rate dropped to 1.7 moles (Fig. 12) when the mercaptan was present and rose to 2.3 moles only on the residual surface (Fig. 15). The rates of carbon monoxide and carbon dioxide formation

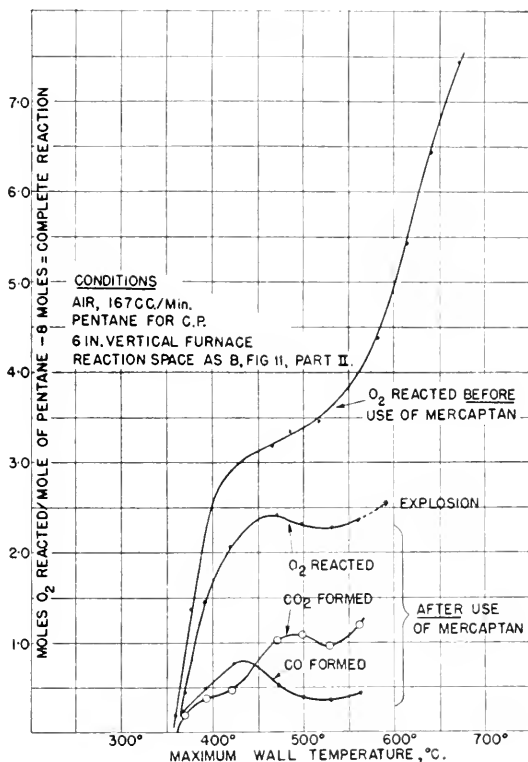


FIG. 15. Graphs showing the effect of the surface of iron sulphide remaining after the use of ethyl mercaptan on the oxidation of pentane in the steel reaction chamber.

on the residual surface are given by the lower graphs of Fig. 15 and comparing them with the graphs of Figs. 13 and 14 for pentane plus the mercaptan it will be seen that change of rates of carbon dioxide and carbon monoxide formation is in accordance with the changes in rates of oxygen reacted.

Conclusions

The experiments described in this section help to confirm that the oxidation of pentane is a heterogeneous reaction and show definitely that it is possible by the use of a catalyst poison to determine whether the antiknock action of metallic dope is due to the effect to inhibit the aldehyde reaction or the effect to promote reaction to final products.

Section V

THE PRO-KNOCK EFFECTS OF LUBRICATING OILS, ETHYL MERCAPTAN, AND HYDROGEN SULPHIDE

An extensive series of experiments, made some years ago by King and Moss (10, 11, 13, 14) demonstrated that lubricating oils when added to engine fuel varied in pro-knock effect. The greatest effect was obtained when the oils were added to doped fuels. Olein or oleic acid in a concentration of 1.0% only in the fuel destroyed almost the entire antiknock effect of nickel carbonyl in the large concentration of 10 cc. per gal. in the fuel, and was of similar effect in respect of iron carbonyl, but a concentration of 12% of olein in the fuel was required to destroy 85% of the antiknock effect of a 12 cc. per gal. addition to the fuel of tetraethyl lead. Castor oil, which is soluble in engine fuel to the extent of about 1½% only, was as effective as olein in destroying the antiknock value of nickel carbonyl, somewhat less effective in respect of iron carbonyl but was found to be of no *antiknock* effect when added to fuel doped with tetraethyl lead. The effect of the rape oils which are soluble in any concentration was similar to that of castor. The mineral oils were quite effective in reducing the antiknock value of the carbonyls but large additions were required in respect of tetraethyl lead even to obtain a relatively small effect.

The variation of the pro-knock effect with the natures of the oils and the metals of the dopes could not be explained in terms of theories based on homogeneous reactions, and little information was available about the effect of the several oils on heterogeneous reactions when the contact surfaces were of iron, nickel, or lead. It was known, however, that olein or oleic acid is a poison in respect of nickel catalysts (18, p. 909). Comment was made accordingly in the published account of the experiments and no further explanation attempted.

Similar engine experiments were made later using ethyl mercaptan and hydrogen sulphide additions to engine fuel instead of lubricating oils. The substances, added in small proportion, destroyed completely the antiknock effects of tetraethyl lead and iron carbonyl and gave rise to further pro-knock effects which will be described later. Again the experimental results could not be explained by accepted theory. The sulphur compounds were known catalyst poisons in respect of the carbon dioxide-steam reaction on iron and nickel surfaces, but an explanation of their pro-knock effect given accordingly would have involved the assumptions that catalytic surfaces were provided in the combustion space by the metallic dopes and that the steam formed on them in the absence of a catalytic poison was responsible for the antiknock effect. The experimental results were, therefore, withheld from publication until experiments could be made on the oxidation of hydrocarbon engine fuel at the high temperature of the 'end gas' and on the effect of sulphur catalyst poisons on the reactions.

Selection of Sulphur Catalyst Poison

It was a convenience to use a liquid compound soluble in engine fuel, and thiophene, carbon disulphide, and ethyl mercaptan were tried. The pro-knock effects of the compounds on straight run aviation petrol doped with 2.0 cc. per gal. of tetraethyl lead when used in the C.F.R. engine with unheated induction, are shown by the graphs of Fig. 16. It will be seen that all three

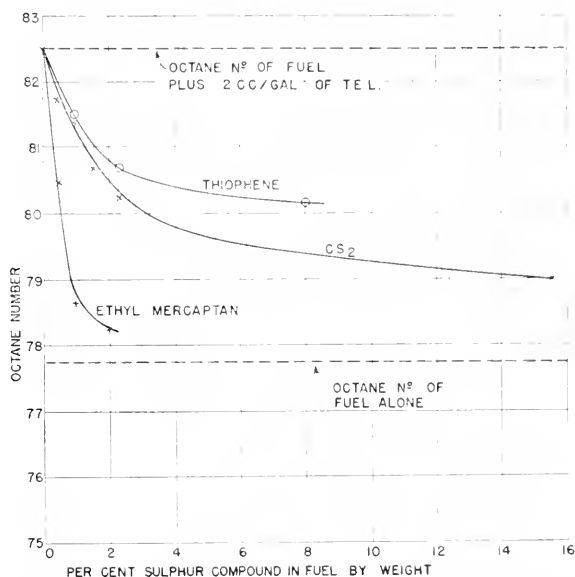


FIG. 16. Graphs showing the pro-knock effect of three sulphur compounds when added to a low octane number engine fuel doped with tetraethyl lead. C.F.R. engine.

substances were pro-knockers and that the mercaptan was outstanding, a concentration of 2% in the fuel being sufficient to destroy nearly all of the effect of tetraethyl lead to raise the octane number of the fuel from 77.8 to 82.5. It was not possible to prevent the loathsome odor of the mercaptan from reaching many parts of the building in which the engine was situated, and hydrogen sulphide was used as an equivalent catalyst poison for further experiments.

Engine Experimental Conditions

The experiments were made with a variety of hydrocarbon fuels used in the C.F.R. research engine. The intake air was unheated in some cases and in others raised to 300° F. as required for the standard method of determining octane number. The knocking tendency of the fuels was generally obtained by the H.U.C.R. method as used in the Air Ministry Laboratory (12), but sometimes by determining octane number. Some experiments were, however, made with very weak or very rich mixtures. Tetraethyl lead was used as the fuel dope in preference to iron carbonyl which on long continued use, especially in large concentration, destroys spark plug insulation and leaves

heavy deposits of oxide in the engine combustion space. The engine experimental results are given by a series of graphs and the experiments are described in succeeding paragraphs.

Hexane Experiments

Experiments with hexane as an engine fuel are of special interest because of the oxidation experiments described in Sections III and IV. The experiments were made with increasing additions of hydrogen sulphide when using either hexane alone or hexane plus 8.0 cc. of tetraethyl lead per gallon and when using correct, rich, and weak mixtures and heated and unheated air supply.

The experimental results are shown by a series of graphs, Fig. 17, H.U.C.R. being plotted against hydrogen sulphide additions. Mixture strengths are

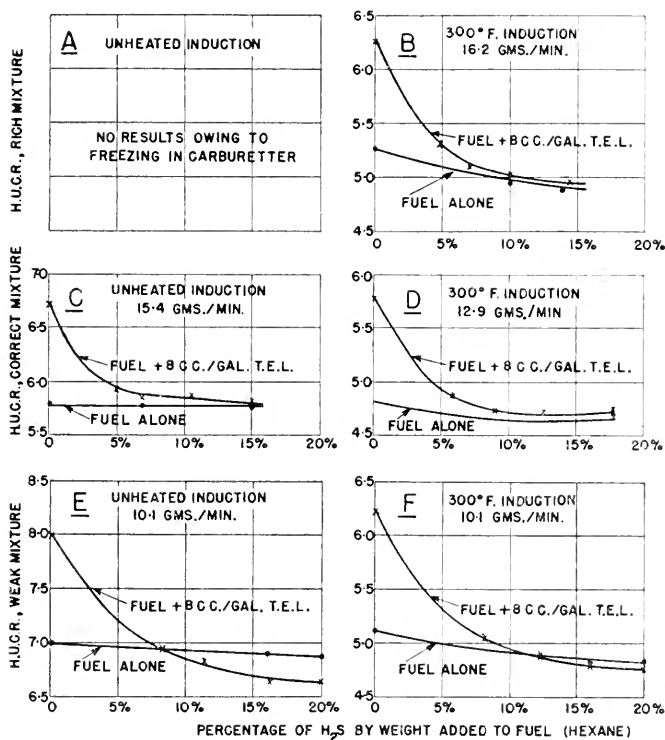


FIG. 17. Graphs showing the pro-knock effect of hydrogen sulphide in respect of hexane doped with tetraethyl lead. C.F.R. engine, for correct, rich, and weak mixtures and heated (300° F.) and unheated induction.

shown by the figures for fuel consumption in grams per minute. Considering first the results for correct mixture strength, Graphs C and D, it will be seen that with unheated induction, Graph C, H.U.C.R. increased from 5.75 to 6.7 on adding the dope to the pentane and then diminished to 5.9 when hydrogen sulphide was added in the concentration of 5%, that is, 85% of the antiknock

value of the dope addition was destroyed. On increasing the hydrogen sulphide addition even to the large concentration of 15% of the weight of the fuel, nothing more happened than the complete destruction of the antiknock effect of the metallic dope.

The engine would not run on hexane at high compression ratios without excessive detonation unless the mixture were very weak or very rich, and results of experiments made accordingly and with heated or unheated induction are given by the Graphs *B*, *E*, and *F* of Fig. 17. The graphs show that by using the hexane at a relatively high compression ratio or with a high induction temperature a small pro-knock effect in respect of the undoped fuel is obtained on adding hydrogen sulphide to the mixture. The explanation advanced is that in conditions of high inlet temperature and high flame temperature due to high compression ratio, the exhaust valve and/or other not well cooled surfaces, such as the piston crown, are raised to the temperature required for the partial oxidation of the end gas to steam and carbon dioxide. The temperature is about 400° C. according to the experiments with a steel reaction chamber, see Fig. 12, and on inhibition of the reaction by hydrogen sulphide the pro-knock effect shown by the experiments would be expected.

A further interesting effect is shown by Graphs *E* and *F*, fig. 17. The graphs cross, showing that the hydrogen sulphide after destroying the antiknock effect of the dope and that due to oxidation of the fuel on hot surfaces carries on to give rise to a further pro-knock effect. The 'further' effect increases as the compression ratio is raised and flame temperature increased accordingly. This will be discussed in succeeding paragraphs.

Aviation Fuel Experiments

The fuel was a high grade straight run Borneo petrol and when used undoped and with *unheated* induction the catalyst poisons were without the pro-knock effect which became evident when metallic dope was added. The experimental results given by the graphs of Fig. 18, obtained with an *induction temperature of 300° F.*, show the double effect already mentioned, that is, the hydrogen sulphide not only destroys the entire antiknock effect of the metallic dope but also the smaller similar effect attributed to the formation of steam and carbon dioxide on combustion chamber surfaces becoming active in the high temperature conditions. The two pro-knock effects obtained on adding hydrogen sulphide in a concentration of about 8% in the fuel suffice to reduce the octane number to 64.5.

Coal Spirit Experiments

The spirit was procured from the low temperature distillation of coal. The octane number was higher than that of the petrol but lead response was less; a 4 cc. per gal. addition of the metallic dope raised the octane number from 75½ to 84, whereas a similar addition to the aviation petrol raised the octane number from 70 to 85. The relatively low concentration of 3% of the hydrogen sulphide was sufficient to destroy the original antiknock effect of the dope, represented by an increase of 8½ octane numbers. The second and third

effects are as described for the engine experiments with hexane but are of greater magnitude and obtained with smaller percentages of hydrogen sulphide.

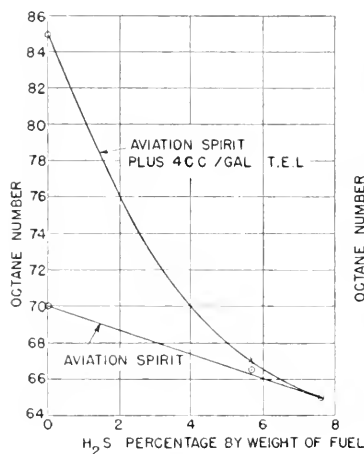


FIG. 18.

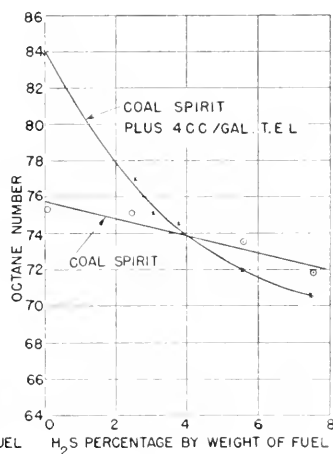


FIG. 19.

FIG. 18. Graphs showing the pro-knock effect of hydrogen sulphide on aviation spirit doped with tetraethyl lead. C.F.R. engine, 300° F. induction temperature.

FIG. 19. Graphs showing the pro-knock effect of hydrogen sulphide on coal spirit doped with tetraethyl lead. C.F.R. engine, 300° F. induction temperature.

Cyclohexane Experiments

The second and third pro-knock effects of hydrogen sulphide are shown by the engine experiments already described to become increasingly evident as the temperature of combustion is raised either by increasing compression ratio or by raising induction temperature. The experiments were, therefore, repeated in conditions requiring the use of compression ratios approaching the limit of the C.F.R. engine. Weak and rich mixtures of cyclohexane were used with induction temperatures of 300° F. and it will be seen by reference to the graphs of Fig. 20 that the highest useful compression ratios were 7.9 and 7.4 respectively in the circumstances. The H.U.C.R. values increased to 10.0 and 9.1 on adding tetraethyl lead to the fuel in the concentration of 24 cc. per gal. The excessive dope addition was used advisedly in an endeavor to determine whether the third pro-knock effect shown by the crossing of the graphs was due to the hydrogen sulphide or to the metallic dope in the presence of the sulphide. It is well known that the specific effect of tetraethyl lead diminishes as the concentration in engine fuel increases and it is probable that no more than one-third of the 24 cc. addition was effective to prevent detonation. The experimental results given by the graphs of Fig. 20 show that (a) The original increase in H.U.C.R. due to the dope was destroyed by about 5% of hydrogen sulphide in the weak mixture and about 2½% in the rich mixture.

(b) The second pro-knock effect of the hydrogen sulphide is more pronounced than in the experiments made at lower compression ratios. Thus the sulphide

in the concentration of 15% reduced the H.U.C.R. of the undoped fuel, weak mixture, from 7.9 to 6.2, that is, an amount equal to 80% of the increase obtained with the large addition of dope to the fuel in the absence of the catalyst poison. Similar effects were obtained for the rich mixture but comparisons cannot be made because the percentage of hydrogen sulphide added to the fuel-air mixture was not large enough to obtain limiting values for the effects.

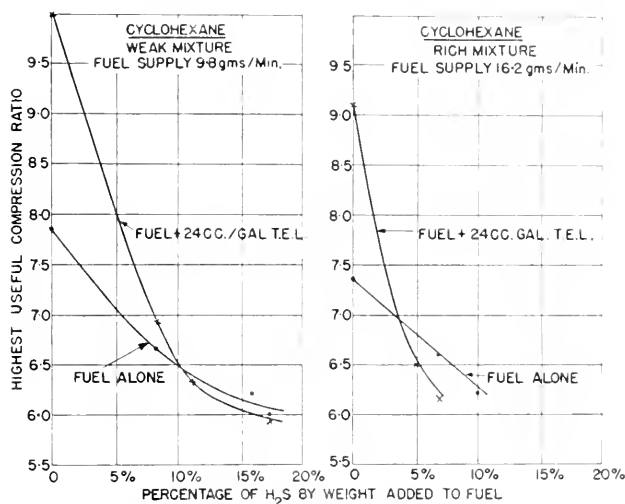


FIG. 20. Graphs showing the pro-knock effect of hydrogen sulphide on rich and weak mixtures. Cyclohexane doped with tetraethyl lead. C.F.R. engine, 300° F. induction temperature.

(c) The third pro-knock effect of the hydrogen sulphide, shown by the crossing of the graphs, is most apparent for the rich mixture for which fuel was supplied at the rate of 16.2 gm. per min. as compared with 9.8 for the weak mixture. The rich mixture in the engine contained, therefore, nearly twice as much dope as the weak mixture, and, since conditions in respect of hydrogen sulphide supply remained unchanged, it is reasonable to suppose that the third pro-knock effect was due in some way to the tetraethyl lead when used at high flame temperatures in the presence of the sulphide.

Benzene Experiments

The experiments with benzene as the engine fuel were undertaken to confirm that, as suggested above, tetraethyl lead becomes a pro-knock if used in conditions of high flame temperature and in the presence of hydrogen sulphide. It is well known that benzene does not detonate in the C.F.R. engine even when the compression ratio is as high as 10. The addition of metallic dope is, therefore, without apparent effect. Experiments were made accordingly at an induction temperature of 300° F. The experimental results are given by the graphs of Fig. 21. They show that when the undoped fuel was used at the high compression ratio of 10, detonation did not occur until hydrogen sulphide had been added to the mixture in the high concentration of nearly 20% by

weight of the benzene. This result confirms that the 'further' pro-knock effect observed in the earlier experiments was not due to the effect of the hydrogen sulphide alone. It will be noted, however, that on adding tetraethyl lead to the benzene in the concentration of 4 cc. per gal. detonation occurred

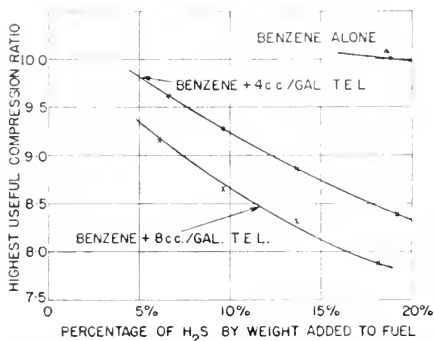


FIG. 21. Graphs showing the pro-knock effect of tetraethyl lead in small concentration in benzene obtained when combustion occurs in the presence of hydrogen sulphide. C.F.R. engine, unheated induction.

and the H.U.C.R. fell to 9.6 when the percentage of hydrogen sulphide in the fuel was 7% only, and further to 8.4 when the percentage was increased to 19. On increasing the concentration of tetraethyl lead to 8 cc. per gallon, a still greater pro-knock effect was obtained as shown by the lower graph of the figure, H.U.C.R. being reduced to 9.1 when the percentage of hydrogen sulphide was about 7, and to 7.8 when it was 18.

Section VI

DISCUSSION OF EXPERIMENTAL RESULTS

Nature of the Reactions Described

It was suggested, Section V, Part II (9), for discussion and further experiment "that the oxidation of pentane is an heterogeneous reaction, velocity depending on the nature of the contact surface and the manner in which the reacting mixture is brought into contact with it". Some further experimental work supporting the general proposition has been described in this Part and will be discussed in succeeding paragraphs.

When pentane is oxidized in reaction chamber No. 10, and the active surface is of clean Jena glass, the usual aldehyde hump appears on the graph for oxygen reacted, see Fig. 3. If now iron carbonyl be added to the reacting mixture, giving an active surface of iron, the aldehyde hump disappears and reaction is almost completely to steam and carbon dioxide (Graph *B* of the figure). Then on allowing the active surface to go to iron oxide by ceasing to supply the carbonyl, the aldehyde hump reappears (Graph *C* of the figure). These experimental results obtained with a flow configuration especially adapted rapidly

to remove oxidation products from the surface on which they are formed give strong support to the view that the oxidation reaction is heterogeneous.

The experiments with ethyl mercaptan give further support to the view mentioned. Thus, the graphs of Fig. 6 for the oxidation of hexane in the glass reaction chamber No. 10 in clean condition show that the aldehyde hump remains when ethyl mercaptan is added to the reacting mixture, indicating that the mercaptan is without effect to alter the surface at the temperature of the experiments. If, however, iron carbonyl be added to the reacting mixture instead of the mercaptan, Fig. 9, and an active surface of iron is deposited on the glass, the aldehyde hump disappears, and oxidation is to carbon dioxide and steam at all temperatures of reaction, as for pentane in similar conditions. If now the active iron surface is converted to the sulphide on adding the mercaptan, the aldehyde hump is not recovered and reaction velocity at all temperatures diminishes to a relatively low rate. The rate may reach zero at temperatures rising to over 500°C . and be inappreciable at higher temperatures in *suitable conditions of flow configuration* as shown by Graph B, Fig. 18, Part II (8). Again it is difficult to interpret the experimental results otherwise than by considering the reactions to be heterogeneous.

The experiments with the steel reaction chamber of relatively large volume, Fig. 12, are also significant. The surface was not of uniform temperature and was in part of iron oxide and in part of iron. The oxidation of pentane in the chamber is, therefore, a mixed reaction yielding, over the low temperature range, aldehyde on the oxide and final products on the iron. On adding ethyl mercaptan to the mixture, the reaction to aldehyde which occurs on the surface of iron oxide as previously shown, Fig. 3, continues but that to steam and carbon dioxide occurring on the iron part of the surface is inhibited, giving the over-all result as shown by the graphs of Fig. 12.

The Negative Temperature Coefficient of Reaction

The negative coefficient depends for its existence on the aldehyde hump which is more pronounced for oxidations in reaction chamber No. 10 than for oxidations in conventional combustion reaction spaces. It is necessary, therefore, in seeking an explanation to remember that in reaction Chamber No. 10 oxidation occurs with great rapidity, time of exposure being of the order of one second, that the high velocity of reaction is due to the flow configuration being adapted to remove surface oxidation products immediately on their formation, that the products do not remain in the chamber and on leaving it to reach the exit are exposed to temperatures lower than that of their formation. The chamber is thus suitable for following the course of reactions occurring at specified temperatures, and the existence of a negative temperature coefficient when pentane is oxidized in the chamber on other than a metal surface indicates that a reaction of high velocity is succeeded, on raising the temperature, by one of lower velocity. Thus referring to the graphs of Fig. 10, Part I (8), it will be seen that carbon monoxide formation reaches a maximum at about 400°C ., the temperature of the aldehyde hump,

and then falls to a minimum at 520° C. The rate of carbon monoxide formation then rises as temperature increases, slowly at first but with great rapidity at temperatures above 600° C. until at 660° C. it exceeds that of carbon dioxide formation. The experimental results show a high reaction velocity over the lower temperature range when the pentane is oxidized to aldehyde, and initially a relatively low reaction velocity at higher temperatures when the pentane is oxidized to carbon monoxide. During the temperature interval between the high velocity, low temperature reaction to aldehyde and the acceleration to high velocity of the high temperature reaction to carbon monoxide, the over-all rate of oxygen reacted reaches the relatively low value which accounts for the negative temperature coefficient. The oxidation of pentane could not proceed in the manner described if the reactions were homogeneous, so conversely the existence of a negative temperature coefficient may be taken as an indication of heterogeneous reactions.

A negative temperature coefficient of reaction was obtained by Pease (16) nearly 20 years ago and was observed when propane was oxidized by a flow method. The experiments of Pease and those of later workers are discussed by Jost in *Explosion and Combustion Processes in Gases*, pages 427-449, English translation by Huber O. Croft, and it is stated, page 449, that many facts support the conclusion that the reaction mechanism differs as between low and high temperature.

Oxidation in the End Gas in an Engine

If oxidation of the fuel in the end gas be a heterogeneous reaction, the anti-knock effect of metallic dope can be attributed to catalytic action, and detonation in the body of the gas cannot be due primarily to any process of oxidation. If, on the other hand, oxidation be a homogeneous reaction, existing theory in respect of the cause of detonation and the antiknock action of metallic dope would be supported. Antiknock action only will be discussed at present although some of the experimental work described in Parts I (8) and II (9) has an important bearing on the cause of ignition and detonation; a subject which it is proposed to discuss in a subsequent Part.

The Revised Positive Catalyst Theory

It is well established that the unburned combustible mixture (end gas) confined between the advancing flame and some part of the surface of the engine combustion space is the seat of detonation, that the *metal* of organo-metallic compounds is responsible for their antidetonation effect, and that turbulence is effective to reduce detonation. The temperature of the end gas in an engine not supercharged and using unheated mixture has been calculated to increase from 670° C. for a compression ratio of 4 to 880° C. for a compression ratio of 10, while the flame temperature may rise accordingly from 2500° to 2750° C., and radiation would be expected to give rise momentarily to high surface temperatures. The conditions as described, although prevailing for a small fraction of a second, suffice for at least partial oxidation of the end gas by flameless combustion. The experimental results for the

laboratory oxidation of doped pentane or hexane given by the graphs of Fig. 8, Part I (8), and Fig. 5 of this Part, in conditions of temperature, turbulence, and time of reaction approaching those prevailing in the combustion space of an engine, show that the metal of the dope deposited on the available surface effects the oxidation of the hydrocarbons to steam and carbon dioxide with great rapidity at temperatures above $500^{\circ}\text{C}.$, as long as the metal surface is maintained by continuous deposition from the organometallic compound. The end gas in an engine is always at a temperature higher than $500^{\circ}\text{C}.$ late in the period of flame travel and the contact surface of the gas probably at a still higher temperature due to radiation from the flame. Doped fuel in the end gas would, in the circumstances, be oxidized with great rapidity to steam and carbon dioxide on the catalytic surface maintained as in the laboratory reaction chamber by continuous deposition of the metal of the dope. The effect of steam especially to reduce inflammability is shown by the experiments described in Section I, and, dilution of the end gas being sufficient, self-ignition ahead of the flame could not occur and combustion would be completed in the normal course without detonation. Verification that the action of metallic dope is as described is obtained by considering the effects of sulphur compounds which are catalytic poisons in respect of the carbon dioxide-steam reaction on metal surfaces. Thus, ethyl mercaptan inhibits the carbon dioxide-steam reaction in laboratory oxidations of doped fuels, as shown by the experiments described in Section IV, and the mercaptan or hydrogen sulphide, when added to doped engine fuel, destroys the antiknock effect of the organometallic compounds as shown by the experiments described in Section V. When hexane undoped was used as fuel in the C.F.R. engine in conditions leading to relatively low flame and engine temperatures, the catalytic poison was of no pro-knock effect even in the large concentration of 15% in the fuel, Graph C, Fig. 17. However, when conditions of engine operation led to relatively high surface temperatures in the combustion space, the consequent steam-carbon dioxide reaction became an antiknock factor because knock occurs on its inhibition by the catalyst poison (see Figs. 18, 19 and 20). The antiknock effect of hot surfaces is most evident at high compression ratios which are necessarily accompanied by correspondingly high flame temperatures. Thus, referring to Fig. 20, inspection of the graphs shows the decrease in H.U.C.R. obtainable by inhibition of the carbon dioxide-steam reaction to be almost as great as the increase obtained on the addition of tetraethyl lead in very large concentration. That is, the tetraethyl lead antiknock effect is added to an existing effect. Both effects are due to dilution of the end gas with the product of a carbon dioxide-steam reaction and both are destroyed by the catalyst poison.

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THE OXIDATION, IGNITION, AND DETONATION OF
FUEL VAPORS AND GASES

IV. THE CAUSE OF DETONATION OR COMBUSTION KNOCK IN ENGINES

By R. O. KING

THE OXIDATION, IGNITION, AND DETONATION OF FUEL VAPORS AND GASES

IV. THE CAUSE OF DETONATION OR COMBUSTION KNOCK IN ENGINES¹

By R. O. KING²

Abstract

A nuclear theory of self-ignition is described which is based on the substitution of finely divided carbon for the nuclear drops of the Callendar theory. The finely divided carbon appears in the gaseous combustible mixture in the engine as a result of pyrolysis of the lubricating oil or of the fuel. The theory is therefore of general application and can be applied to explain combustion knock or detonation when permanent gases such as hydrogen as well as hydrocarbon vapors are used as fuel for the carburetor type of internal combustion engine. The theory is supported by experimental evidence quoted mainly from earlier publications and is intended as a working hypothesis for further confirmatory experiments.

Introduction

The experiments described in preceding Parts were directed mainly to ascertain the cause of the effect of metallic dopes to delay the onset of detonation in engines. They support the view that delay or prevention is due to dilution of the end gas by the products, steam and carbon dioxide, of an oxidation reaction occurring on the surface of the combustion space made 'active' by metal deposited on the thermal decomposition of the dope. The detonation delaying effect of dilution would operate whatever the cause of detonation, and discussion of that effect was therefore withheld pending a description of especially related experiments. Some of the experiments have been completed and others are in progress. It is hoped to describe all of them in succeeding Parts. It will, however, be of assistance to the reader and save space later if the working hypothesis used to plan the experimental work is given separately in this Part after a brief review of recent theory.

Section I

The Callendar Nuclear Theory of Self Ignition

The continued propagation of flame in a combustible mixture after ignition at a point depends, according to the classical theory, on the rate of heat generation by combustion continuing to be greater than the rate of loss by conduction, convection, and radiation. The theory does not provide an adequate explanation for the sudden increase in flame velocity in a tube after a certain distance has been traversed by the flame front or the similar effect in the combustion space of an engine. In fact, ignition of the unburned gas well ahead of the flame front, that is, self-ignition, can be obtained in

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suitable conditions of temperature and pressure. Self-ignition of the end gas in an engine results in detonation, indicated by combustion knock which occurs also if the rate of flame propagation become abnormally great.

A nuclear theory of self-ignition was advanced by Callendar (7, 8) to explain the occurrence of detonation in an engine and the antiknock effect of metallic dopes. In the particular case of ordinary liquid hydrocarbon fuels, always containing some proportion of high boiling point constituents, it was considered that the nuclei would be liquid drops of the higher boiling point fractions remaining after evaporation of the lighter fractions of the fuel. These residual drops, as they evaporate, would be contained within a shell of nearly pure vapor which would recondense in part as the compression pressure was raised because hydrocarbon vapor, unlike steam, tends to condense on compression. Vaporization would thus be retarded and the drops could persist until late in the period of combustion. The drops, being surrounded by vapor of the high boiling point constituents of the fuel, would have a lower ignition temperature than that of the gaseous mixture in which they were dispersed. Thus if the end gas were impregnated with liquid drops, nearly simultaneous ignition (detonation) might occur prior to the completion of combustion of the gas in the normal course of flame travel.

Hydrocarbon fuels completely vaporized and mixed with air in combining proportions present some difficulties because condensation during compression could not occur in the circumstances. Callendar suggested that in such cases the smoke particles which are always present in the operation of an internal combustion engine would serve as foci of condensation and "with the aid of such carbon nuclei, drops of a highly ignitable nature may continue to exist or *may be formed by condensation* at temperatures such that the mixture should be completely vaporized according to the ordinary rules of calculation."

The possibility that carbon nuclei as such might be effective centers of ignition in an otherwise homogeneous gaseous combustible mixture was not discussed. The carbon nuclei mentioned as being present in the engine combustion space were the smoke particles remaining from the previous combustion of hydrocarbons, and it was suggested only that they could promote the *formation of liquid drops* in a completely vaporized mixture by serving as foci of condensation.

Aside from the failure of the nuclear drop theory to account for detonation in completely vaporized mixtures, there appeared to be some doubt about the drops being present in sufficient concentration in the end gas to provide an igniting effect, and Callendar's suggestion that the metallic dope prevented ignition of the drops by plating them with metal, thus preventing absorption of radiation from the flame, was not convincing. The chemical side of the problem was therefore explored at his request but with the fixed idea that some product of the oxidation of the rich mixture surrounding the slowly evaporating drops would be readily inflammable and thus ignite the drops.

Oxidation, according to the Armstrong-Bone hydroxylation theory, then generally accepted, would begin with the formation of an alcohol and proceed by further oxidation to aldehyde, carbon monoxide, steam, and carbon dioxide. All the oxidation products mentioned, except the aldehyde, were known to delay detonation. A number of aldehydes were tried as additions to engine fuel but proved to be of inappreciable effect on detonation (5, p. 183; 6, p. 20). The idea that detonation must be due to the accumulation of some oxidation product in the nuclear drops was however not abandoned. It was known that certain unstable organic peroxides decomposed with some violence on heating, and it was suggested (by Mardles) that a peroxide instead of an alcohol might be the primary oxidation product. The suggestion fitted exceptionally well into the nuclear drop theory, and, as the result of numerous confirmatory experiments, Callendar concluded (5, 6), in respect of *paraffinic fuels and ether*, that although the amount of peroxide formed would not in itself be sufficient to cause the detonation observed it would act as a primer for the simultaneous ignition of the nuclear drops—and detonation thus caused would be prevented if metallic dope were concentrated in the drops owing to the reduction of the peroxide by the metal of the dope.

It will be noted that the nuclear theory remained encumbered by liquid drops and, although it could not be accepted as having more than a limited field of application, the idea that organic peroxides were responsible in some way for fuel detonation in engines received fairly general approval in large part because it seemed to pave the way for the application of chain reaction theories to combustion as it occurs in the engine.

Section II

Chain Reaction Theory

A nonhomogeneous combustible mixture is a necessary prelude to self-ignition, according to the nuclear theory. The chain reaction theory was devised to account for oxidation leading to ignition in a homogeneous mixture, reaction being between single molecules. Experimental evidence in support of the theory has been generally obtained by using reacting mixtures not diluted with nitrogen, at relatively low pressures and without taking flow configuration (15) into account. Nevertheless many attempts have been made to use the theory to explain the mechanism of oxidation and detonation in the turbulent fuel-air mixtures used in engines at the extremely high pressures attained during combustion of the end gas, although mixtures so diluted with nitrogen cannot be detonated in tubes.

There is little agreement about the manner of initiation of chain reactions and still less about the mechanism of the reaction. It is most simple to suppose, as suggested by Mardles (5, 6) and by Moureu, Dufrasse, and Chaux (18), that a collision between a fuel and an oxygen molecule results in the formation of a peroxide having a relatively high energy content, and Egerton (9) considers that reactivity is handed on from the peroxide to new reactant

molecules, the reaction being autocatalytic in character, a view that is not in accordance with the Armstrong-Bone hydroxylation theory in support of which there is considerable experimental evidence if reaction occur at high pressure. Egerton considers that the metallic antiknocks delay oxidation by forming metallic peroxides that react with and destroy the fuel peroxides, thus breaking the reaction chains and preventing detonation.

Norrish (19) considers the peroxidation theory to be unsatisfactory and suggests that reaction chains start from the aldehyde and proceed by an "atomic chain" mechanism according to which methane for example would be oxidized by a chain reaction involving free radicals and atomic carbon. Oxidation of other hydrocarbons requires atomic oxygen as a link in the chain reaction. Norrish, to a considerable extent, avoids conflict with the hydroxylation theory of oxidation but does not, in the reference given, apply his chain reaction theory to explain the action of metallic antiknocks.

Rice (21) considers that thermal decomposition results in the replacement of one molecule of hydrocarbon by several, with the result that the increase in concentration may greatly augment rate of oxidation and increase knocking tendency accordingly, oxidation being a chain reaction involving free radicals. Metallic antiknocks are assumed to cause the fuel molecule to decompose into relatively few small molecules and in this way reduce knock. Rice appears to envisage a limited decomposition, unlike Norrish who assumes decomposition to carbon or oxygen atoms.

Steele (23) suggests that hydrogen liberated by the decomposition of hydrocarbons during the combustion period in the engine is responsible for fuel knock. He considers this view to be supported by the engine experiments of A. F. Burstall showing that hydrogen gives rise to violent knock (4) while carbon monoxide does not knock in any circumstances (3). It is further suggested by Steele that the knock due to hydrogen liberated by decomposition of the hydrocarbon can be prevented by adding more hydrogen to carry the partial pressure out of "a critical range."

Boerlage and Van Dyck (1) established a relation between the *initial* cracking speeds of Diesel engine fuels and the cetene numbers with a considerable degree of success. An attempt to establish a relation between the *initial* cracking speeds of fuels used with carburetor engines and octane numbers was less successful. The initial cracking speed of iso-octane which is at the top of the octane scale was, for example, greater than that of heptane which is at the bottom of the scale. The initial cracking speed of heptane was however greater than that of some hydrocarbons of a higher octane rating. The experiments were made at atmospheric pressure and conditions were not the most suitable for cracking the hydrocarbons to carbon. The experimenters assumed that detonation depends on a high rate of oxidation in a homogeneous mixture of hydrocarbon vapor and air, and were most concerned with the gaseous products of cracking in an endeavor to determine the conditions in which free radicals or an active form of oxygen would be present and initiate chain reactions.

The above brief review of chain reaction theory as applied to combustion in the engine is admittedly superficial. It has been given to illustrate in some degree the difficulties met with in applying the theory to explain the cause of detonation in an engine and the action of antiknocks. The metallic antiknocks decompose at temperatures reached before the end of compression and the metal, which is generally agreed to be the active agent to prevent knock, is deposited mainly on surfaces. It is difficult to understand how this metal can be present later on to break reaction chains in the end gas. Similarly it is difficult to understand how organic peroxides, which by definition are initial and unstable products of slow oxidation at relatively low temperatures, can persist and be essential links in chain reactions occurring at the extremely high temperatures of the end gas. The Callendar nuclear drop theory did at least provide a means of their persistence. Finally, Egerton in a lengthy discussion of "Existing knowledge on knocking and its prevention" (10), states "although it would be generally agreed that in the oxidation of saturated paraffins, reaction chains are operative, there is as yet no agreement on the mechanism of the process or the nature of the chain carriers."

Section III

Heterogeneous Oxidation Reactions and a Revised Nuclear Theory of Self-Ignition

Outline of Theory

The experiments described in preceding Parts indicate that flameless oxidation of fuel in mixtures with air in engine conditions occurs solely on hot surfaces, not in the body of the gas by a chain reaction process. The surfaces in the combustion space of an engine may comprise areas of metal, metallic oxides, adherent carbonaceous matter, or carbon distributed in the combustible mixture as fine particles. When the surfaces reach a suitable temperature oxidation may be to partial or final products in accordance with the nature of the surfaces and the degree of turbulence. The heat of reaction does not suffice to start a flame if surface temperature is controlled by water or air cooling, and combustion after spark ignition proceeds to completion without the occurrence of pre-ignition or detonation. It is to be noted that the temperature of containing surfaces can be controlled but not that of the surfaces of material nuclei in the body of the gas.

Flame may, however, be started without spark ignition if a surface become so thickly coated with carbon that external cooling is ineffective or if insufficiently cooled points or small areas become incandescent. Flame may also be started by the combustion of aldehydes which are formed in great profusion in conditions of excessive turbulence, and can be ignited by contact with surfaces at the temperature attained in high duty engines by the exhaust valve. Thus methyl and ethyl alcohols, which oxidize in the first stage to aldehydes, are especially prone to pre-ignition when used as engine fuel for the Ricardo E35 engine in spite of the cooling effect arising from the high latent heat of evaporation.

Flame started in any of the ways mentioned moves through the combustible mixture just as if it had been started by an electric spark and does not give rise to detonation. If the flame starts before the passage of the spark it is described as pre-ignition and if timing is approximately correct the engine will run without spark ignition.

Detonation as it occurs in an engine using hydrocarbon fuel can be initiated solely if flame be started nearly simultaneously at points distributed throughout the end gas, and experiments indicate that the conditions required are governed by the temperature and pressure of the gas and the concentration in it of carbon nuclei, the concentration being determined, other things being equal, by the pressure. The theory will now be discussed in greater detail.

End Gas Temperature and Pressure

The temperatures and pressures attained by the end gas at compression ratios extending from 4 to 10 : 1 given in Table I below are calculated on the basis that detonation occurs when the combustion pressure reaches 90% of the maximum value.

TABLE I

END GAS TEMPERATURES AND PRESSURES, RICARDO E35 VARIABLE COMPRESSION ENGINE

Compression ratio	Initial compression pressure	Initial compression temperature, ° C.	90% of max. combustion pressure, lb./sq. in.	Calculated temperature of end gas, ° C.
4 : 1	Atmospheric	133	346	673
5 : 1	"	112	477	707
6 : 1	"	102	616	741
7 : 1	"	95	—	765
8 : 1	"	90	—	809
10 : 1	"	—	—	877

The data used to compile the table are from published performance figures in respect of the Ricardo E35 variable compression engine (5, p. 211; 6, p. 26; 20). The end gas temperatures were calculated taking the value of γ to be 1.36. This allows for the end gas receiving some heat during the combustion period. If the temperature at the end of compression by the piston were required, the value of γ would be taken to be 1.34. The end gas temperatures for compression ratios of 7 to 10 : 1 are extrapolated values, indicator diagrams not being available. It will be noted that end gas temperature is very nearly a linear function of compression ratio, and, evaluating the constants, — end gas temp. = $(34 \times \text{C.R.} + 537)^\circ \text{C.}$

Nuclear Ignition

The Callendar theory of self-ignition was based on the nuclei, dispersed in a combustible gaseous mixture, having a lower ignition temperature than the otherwise homogeneous gas (7, 8). It was, however, shown by the later experiments of King (16) and King and Mole (17) that the nuclei need not

be of a combustible substance. Fine drops of water, stone dust, or powdered metallic oxides are all effective explosion agents. A description of experiments showing the igniting effect of a variety of nuclei in respect of mixtures of hydrogen, ethylene, and methane is given in the references quoted. Similar igniting effects were obtained at the time, in respect of carbon monoxide and acetylene. Experiments made later, with the arrangement of apparatus described in the references, in the Colloid Science Department, Cambridge University, demonstrated that pentane-air mixtures were especially sensitive to ignition by nuclei. When the mixture was supplied to the combustion tube at the rate of 300 cc. per min. explosion occurred at $570^{\circ}\text{C}.$, but nuclei such as finely divided silica caused explosion at $450^{\circ}\text{C}.$ and the still lower explosion temperature of $350^{\circ}\text{C}.$ was observed when the nuclei were fine particles of nickel oxide. Carbon was found to be an effective igniting agent but the variety used was so finely divided that the particles tended to stick together and float about instead of falling rapidly through the heated mixture. The cause of the effect is still a subject of speculation but there are two possibilities, one chemical, the other electrical. A reasonable chemical explanation is that the nuclei provide surfaces in the gas on which oxidation can occur, with the consequence that the heat of reaction would raise the temperature sufficiently to start a flame. It is difficult to apply this explanation to a particle of water, which would be evaporated to steam in the process. An electrical explanation seems to apply better to drops of water. It is known that such drops become positively electrified when falling through air even at atmospheric temperatures, and the potential of the charge would increase as the surface area decreased as evaporation proceeded. It is not impossible that ignition is electrical in some cases and due to the heat of chemical reaction in others. However, considering combustible nuclei such as carbon particles which, as will be shown in a subsequent Part, are especially effective to ignite combustible gaseous mixtures, it is reasonable to suppose that flame is started by the heat of the oxidation reaction even if the hot carbon particles which are pyrophoric, are themselves insufficient. Thus, with reference to Table I, the temperature of the end gas late in the period of combustion in an engine exceeds $600^{\circ}\text{C}.$ even at the low compression ratio of 4 : 1. Carbon particles derived from cracking of hydrocarbon fuel would be red hot in the circumstances and tend to start a flame in most combustible mixtures even if temperature were not further increased by oxidation of the gas in contact with them and by radiation from the advancing flame. At the relatively high compression ratio of 6 : 1 temperature in the end gas exceeds $700^{\circ}\text{C}.$, Table I, and the carbon particles would be in an active state of combustion.

Carbon Formation in the Engine Combustion Space

Pyrolysis of the lubricating oil yields free carbon. The carbon may be contained in part in sticky substances tending to adhere to surfaces and in part as fine particles which appear in the exhaust when the lubricant passes the piston at an excessive rate. The extent of the formation of adherent

carbonaceous matter, rather than of free carbon distributed throughout the combustible gaseous mixture, depends on factors such as the natures of the lubricant and of the fuel as well as mixture strength. Free carbon derived from the lubricating oil would be distributed throughout the whole of the combustible mixture, not especially concentrated in the end gas. Detonation is therefore not attributed to ignition by such carbon nuclei. They may, however, act to increase rate of flame propagation.

A second source of free carbon is found in the cracking of fuel molecules in the flame front. Thus Haslam and Russell (14), referring to the combustion of hydrocarbons, state that "under ordinary combustion conditions there is a race between thermal decomposition or "cracking" and the process of hydroxylation (oxidation). If the conditions favor oxidation there will be no soot. On the other hand if the conditions favor cracking the hydrocarbon will decompose into carbon and hydrogen and will burn with a smoky flame." The conditions in the engine favor cracking. Thus the flame as it moves through the combustible mixture, impinges on relatively cool surfaces and the formation of soot would be expected. The conditions are in fact similar to those used to procure 'acetylene black' from the burning gas, and it is significant that although the molecule of acetylene is thermally stable at end gas temperatures when the gas is diluted with nitrogen (22), yet the gas cannot be used as engine fuel even at low compression ratios because of the violence of detonation. It may be concluded therefore that free carbon is carried into the end gas by the turbulence which always accompanies the movement of flame and provides the distributed ignition centers required for detonation.

The third source of free carbon, namely the cracking of the end gas, provides ignition nuclei just where required to promote detonation. There is however little information available in respect of the rate of carbon formation when pentane and other hydrocarbons usually present in fuel for carburetor engines are decomposed at the temperatures and pressures of the end gas as given in Table I. It was observed by Callendar and associates (5, 6) that the combustion of paraffins ranging from pentane to undecane was accompanied by a fine persistent fog, some of which passed through the train of absorption apparatus. Similar effects were observed during later experiments and quoting from notes made at the time and referring to the combustion of pentane "Both oxidation and decomposition became appreciable at 300° C. A feature is that decomposition is delayed if oxidation proceed rapidly but on the other hand a rapid rate of decomposition as indicated by the volume of smoke issuing from the combustion tube is a sure indication of a slow rate of oxidation." It appears therefore that the relation between hydrocarbon oxidation and decomposition reactions in flameless combustion is similar to that described by Haslam and Russell in respect of combustion in a flame, as already mentioned.

Decomposition of the paraffins lower than pentane was carried out by Hague and Wheeler (13) in a silica vessel at the temperature of 950°C . Methane, which is a non-knocking fuel, yielded a trace only of carbon. Ethane, propane, and butane yielded, respectively 13.9, 11.3, and 19.6% of carbon. The initial cracking temperature of butane was found to be 435°C ., and it may be concluded that the higher paraffins used as engine fuel begin to decompose at still lower temperatures to yield some proportion of free carbon.

Egloff (11) states that the thermal decomposition of pentane has been meagerly investigated but that slow decomposition seems to begin below 400°C . and refers to the "ever present carbon." Similar comment is applicable to hexane.

In view of the lack of data in respect of the pyrolysis of the liquid hydrocarbons commonly used as engine fuel, it is fortunate that especially useful results having a direct bearing on the validity of the nuclear theory of ignition were obtained incidentally by Tizard and Pye (24) during experiments on the ignition of such hydrocarbons by sudden compression. The experiments were directed toward measuring the delay period before ignition and explosion would occur in a hydrocarbon-air mixture compressed to a temperature such that ignition would occur eventually. It was always found that, when an explosion was sharp, combustion was not complete, a fluffy deposit of carbon being thrown down although oxygen was in considerable excess.

The question at issue so far as the nuclear theory is concerned is what came first, decomposition to form ignition nuclei of finely divided carbon or ignition due to a homogeneous oxidation reaction. The question seems to have been answered by the experimental results. Thus the delay period was shortened if, by lack of preliminary cleaning, finely divided carbon was already present in some concentration. Moreover, it is generally agreed that the combustion of hydrocarbons does not involve the preferential oxidation of the hydrogen in the molecule and, accordingly, the carbon found by Tizard and Pye was due to the fact that pyrolysis preceded ignition.

Relatively low temperatures of ignition by compression were observed, values depending on whether ignition temperature were taken as the maximum that had been attained by some part of the compressed mixture or the estimated mean temperature. The mean values for pentane, hexane, heptane, and octane, respectively were 336° , 306° , 292° , and 275°C . Thus, all the paraffin hydrocarbons tried yielded finely divided carbon by pyrolysis at or below the temperatures mentioned.

Higher members of the paraffin series beginning with gas oil are commonly used as cracking stock. Carbon formation was especially troublesome in early methods. Brooks (2, pp. 2078-2087), referring to the Burton process by which the cracking of gas oil or other distillates was carried out at temperatures of about 420°C . and pressures of about 95 lb. per sq. in., states that after treatment of every batch it was necessary to open the still and scrape the carbon off the bottom.

Characteristics of Knocking Combustion as Shown Photographically by Withrow and Rassweiler (25)

The photographs of successive stages of combustion in an engine were taken by a high speed camera developed in the Research Laboratories Section of General Motors Corporation. A set of 30 of the pictures showing knocking combustion is reproduced as Fig. 1 from prints off the original negatives, supplied by Dr. T. A. Boyd, Head of the Fuel Research Section. The pictures are shown in the order taken, reading from left to right and down, starting at 29° before and finishing 40.6° after top dead center (T.D.C.). The engine speed was 900 r.p.m., the compression ratio 4.7 : 1, and the fuel a gasoline having an octane number of 48. The photographs were taken through a flat fused quartz plate 0.75 in. thick covering the combustion chamber which was therefore a non-turbulent type and most suitable for observations of orderly flame movement. It is of interest to interpret the characteristics of combustion shown by the photographs in the light of the revised nuclear theory of ignition stated in preceding paragraphs.

The igniting spark appears at 24.2° before top dead center but flame is not easily visible until 7.2° later. It spreads rapidly during the period 14.6° to 2.6° before top dead center apparently on the carbon nuclei necessarily present in the combustible mixture, and the consequent speckled appearance with the growth of bright spots is the outstanding feature of the period. A change to solid luminescence then begins and is complete at 2.2° after top dead center. That is, 19.2° of crank angle, a time interval of 0.00356 sec. at 900 r.p.m., has been required for the propagation and building up of flame to the stage of solid luminescence. The time interval would be 0.00485 sec. if taken from the passage of the spark.

The temperature and pressure of the unburned gas ahead of the flame front has been increasing during the time interval mentioned above and also the concentration of carbon nuclei. Auto ignition in the end gas is obtained accordingly and shows in the picture taken 0.2° before top dead center near the end of the combustion space over the piston and separated from, and as far ahead of, the flame front as is possible in the confined space. The next picture taken less than 0.0005 sec. later shows that spontaneous combustion has occurred through the whole of the end gas except for a very small area lying just ahead of the flame front. The picture next in order shows the end gas completely filled with flame again of a speckled appearance as would be expected according to the nuclear theory.

It is of interest that the burning mixture ahead of the flame never exhibits the solid luminescence characteristic of the final stage of combustion behind the flame front. A speckled appearance persists, indicating that combustion of the carbon particles responsible for detonation is not completed, and, as would be expected, puffs of black smoke are seen in the exhaust of an engine on the occurrence of detonation knock as distinct from combustion knock.

Furthermore it is well known in engine practice that a non-knocking 'correct' mixture burns with a nearly colorless flame and that it becomes white and luminous if detonation occur. Withrow and Rassweiler, for example, found it necessary to use a considerable proportion of benzene in the fuel mixture in order to obtain photographs of a non-knocking combustion or of the flame movement prior to knock.

Another matter of interest is the incandescent carbon appearing in bright patches mainly around the inlet valve, top left-hand corner of the pictures. It can be seen first in the picture taken at 14.2° after top dead center and continues to glow throughout subsequent pictures, remaining incandescent after combustion of the gaseous mixture is substantially complete.

It is also of interest to compare the explosion times in an engine combustion space with those observed by Fenning for explosions in a bomb (12). The bomb was cleaned between explosions by blowing out with air and there was of course no lubricating oil. There would therefore be no carbon nuclei in the combustible mixture at the time of ignition by the spark, and such nuclei as would be formed by pyrolysis of the hydrocarbon would not appear until late in the explosion period. In the circumstances the period of time between the passage of the spark and the attainment of maximum pressure when using a nearly 'correct' air-petrol mixture was 18 times that observed by Withrow and Rassweiler in the engine combustion experiments just described. Moreover Fenning did not obtain detonation until the mixture was made overrich in petrol, 10.7 to 1, air-petrol, a circumstance promoting the formation of carbon by pyrolysis in the mixture ahead of the flame. The explosion time could not then be observed because the indicator mirror was knocked off the pivots. However, in a 12.9 to 1 air-petrol mixture which just did not detonate, the explosion time was 0.0682 sec. as compared with the 0.0780 sec. observed when the mixture was nearly 'correct'.

The relatively long explosion time in a bomb is usually attributed to the degree of turbulence in the mixture being less than in engine conditions, but in the Withrow and Rassweiler experiments the engine speed was 900 r.p.m. only, the combustion space was not of a turbulent type, and the photographs do not show any mass movement of the burning mixture until late in the combustion period. The conclusion is that the extremely high rate of flame propagation in an engine is due in large part to the carbon nuclei necessarily present throughout the combustible mixture.

Conclusions

The revised nuclear theory of self-ignition, which substitutes carbon particles due to pyrolysis for the liquid drops of the Callendar theory, is complementary to the revised theory of surface oxidation developed in Parts I, II, and III to account for the effect of metallic antiknocks to delay or prevent detonation in carburetor engines using hydrocarbon fuels. Thus the

PLATE I

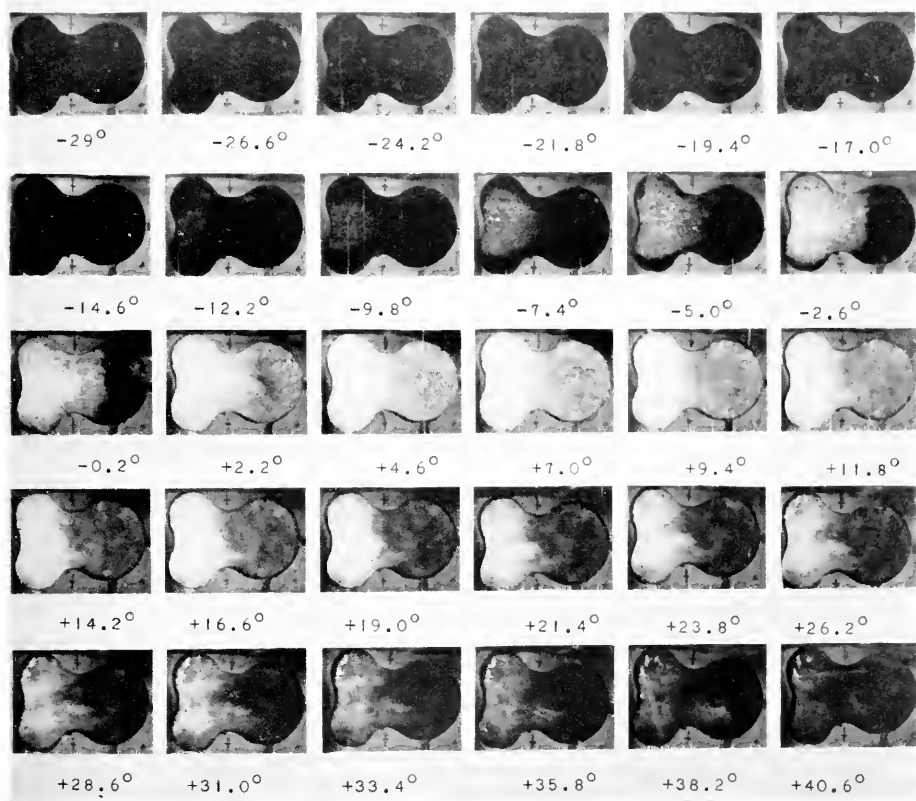


FIG. 1. Photographs of knocking combustion in an engine, taken by Withrow and Rassweiler over the period 20° before to 40.6° after top dead center at intervals of 2.4° of crank angle, engine speed 900 r.p.m.



unburned mixture ahead of the flame is subjected simultaneously to pyrolysis and to oxidation on the contact surfaces. The extent of the heterogeneous oxidation reaction and the nature of the products depends on the degree of turbulence in the mixture, the nature and temperatures of the surfaces, and the combustible mixture. The products of the reaction may be aldehyde, carbon oxides, and steam in varying proportions and are carried into the body of the end gas by turbulence and can be detected therein by chemical or spectroscopic methods of analysis. The end gas, diluted accordingly, tends to become noninflammable by finely divided carbon when the nature and temperature of contact surfaces are such that steam and carbon dioxide constitute a large proportion of the products of the heterogeneous reaction. That is, whether or not detonation occur in particular conditions depends on the result of a race between pyrolysis and a heterogeneous oxidation reaction. Detonation may be described in popular terms as differing from the familiar dust explosion solely in that the combustible dust is distributed in an ignitable mixture of air and gaseous fuel instead of in air only.

Acknowledgments

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THE OXIDATION, IGNITION AND DETONATION OF FUEL
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V. THE HYDROGEN ENGINE AND THE NUCLEAR THEORY
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THE OXIDATION, IGNITION AND DETONATION OF FUEL VAPORS AND GASES

V. THE HYDROGEN ENGINE AND THE NUCLEAR THEORY OF IGNITION¹

By R. O. KING,² W. A. WALLACE,³ B. MAHAPATRA⁴

Abstract

It should not be possible, according to the nuclear theory of ignition, stated in Part IV, to obtain ignition in the body of a gaseous combustible mixture by any method of heating if it remain truly homogeneous while the temperature is raised. Such mixtures cease to be homogeneous when heated by sudden compression to the temperatures required for ignition because of the formation of finely divided carbon by pyrolysis of lubricating oil or of hydrocarbon vapor. The finely divided carbon provides nuclear centers of ignition in the gaseous mixture. Ignition due to finely divided carbon produced by pyrolysis of the lubricant is demonstrated by experiments with hydrogen as the fuel for a C.F.R. engine. The usual pre-ignition and severe knocking were obtained when the engine in normal condition was run on hydrogen, and it was impossible, as previously found by others, to use any but weak mixtures even at low compression ratios. When however the combustion space was decarbonized and thereafter maintained reasonably clear of fluffy carbon, hydrogen could be used as the sole fuel at any compression ratio up to the limit of 10 : 1 possible with the engine, and at any mixture strength ranging from very weak to very rich, while power output varied accordingly. Conversely pre-ignition and combustion knock reappeared when carbon dust was admitted with the combustible mixture.

Introduction

Hydrogen-air mixtures when used in an Otto cycle engine are heated by sudden compression and by contact with hot surfaces such as exhaust valves. The tendency of the mixture to 'detonate' or to explode prematurely in the usual conditions of operation limits the power and efficiency to relatively low values. Ricardo (12), using the E35 engine, cylinder diameter 4.5 in., found that if the mixture with air contained 50% only of the hydrogen required for combining proportions, a compression ratio of 7 : 1 could be used and the high thermal efficiency of 37.5% obtained. It was necessary to lower the compression ratio progressively as the hydrogen concentration was increased but even so it was not possible to use the mixture strength for maximum power. "If an attempt were made to run with a rich hydrogen-air mixture, violent pre-ignition occurred, accompanied by firing back in the carburetor, which rendered further running impossible. Even with the compression ratio lowered to 3.8 : 1 the same thing occurred". There seemed to be a limiting indicated mean effective pressure (I.M.E.P.) of 74 lb. per sq. in. Attempts to obtain higher values by increasing hydrogen concentration or by raising

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the compression ratio were always defeated by the onset of detonation or pre-ignition. The range of mixture strength usable with various engine fuels was discussed by Ricardo in a later publication (13, pp. 42-43) and, in respect of hydrogen, it was stated that "the range of burning could not be explored because, so soon as any excess of hydrogen was admitted, back firing occurred through the inlet valves". Ricardo's conclusions were confirmed by A. F. Burstall (1) even in respect of the I.M.E.P. having a limiting value of approximately 74 lb. per sq. in. The experiments of Egerton, Smith and Ubbelohde (4) with hydrogen as fuel for a Delco knock testing engine, cylinder diameter 2.5 in. only, demonstrated that knocking combustion was not restricted to engines having relatively large cylinders. Egerton (4, p. 517) attributed the detonation to nitrogen peroxide formed from the nitrogen of the air.

The combustion phenomena described by Ricardo and others are usually attributed to ignition of the hydrogen-air mixture by hot surfaces or to ignition being the final result of a chain reaction proceeding at the temperature attained by sudden compression. An alternative explanation is afforded by the nuclear theory of self ignition advanced in Part IV (10), the finely divided carbon for nuclear centers of ignition, as required by the theory, being provided by pyrolysis of the lubricating oil. Experiments made accordingly in the Heat Engine Laboratory of the University of Toronto and described in Section I show that hydrogen can be used as the fuel for an Otto cycle engine, in any mixture proportion with air and at compression ratios rising to 10 : 1, without pre-ignition or detonation if the concentration of finely divided carbon in the gaseous mixture be maintained at a relatively low value.

Section I

Experimental

The Co-operative Fuel Research Committee (C.F.R.) knock testing engine was used for the experiments with hydrogen. The bore is 3.25 in. and the stroke 4.5 in. The compression ratio can be varied from 4 to 10 : 1. The cylinder is maintained normally at a nearly constant temperature of 212° F. by the evaporation of distilled water at atmospheric pressure. The engine is connected to a d-c. main generator and to a similar auxiliary generator. Speed is controlled manually by adjusting the field excitation of the main generator and the electrical output absorbed by a resistor bank.

Lubrication.—The piston is fitted with three pressure rings and one oil scraper ring. A partial vacuum is created in the crank case by fitting the breather with a nonreturn flap valve that closes during the compression and exhaust strokes. The rate of oil consumption in the circumstances is so low that, after 100 hr. running, careful measurement is required to determine the quantity used. The oil in the crank case was maintained at a temperature of between 120° and 130° F. by a manually controlled electric heater. A commercial brand of S.A.E. 30, without 'additives', was used during the experiments.

Hydrogen Supply.—The standard horizontal carburetor with 9/16 in. diameter venturi and no throttle plate was used for the experiments. Hydrogen was admitted to the throat of the venturi through a 0.125 in. diameter hole in a screw which replaced the standard hold down screw of the unused cap jet. Hydrogen procured by electrolysis was supplied in the usual pressure bottles by the Dominion Oxygen Company, and contained not more than 0.3% of oxygen. The hydrogen passed through an adjustable pressure reducing valve, then through a fine adjustment needle valve to a circular square edged metering orifice in a thin plate and thence to the carburetor venturi. The rate of supply to the engine was taken to be proportional to the square root of the pressure difference, in inches of water, across the orifice.

Air Supply.—Air was taken in by the engine at laboratory temperature and the humidity not controlled. The standard air inlet to the carburetor comprises a short piece of $1\frac{1}{4}$ in. I.D. tubing ending in a 90° elbow into which is fitted a long inlet pipe ($20\frac{1}{2}$ in.) also $1\frac{1}{4}$ in. diam. Eight inches of the outer end is arranged as a silencer but the diameter of the tube is not reduced. The standard pipe inlet was on occasion replaced by a swirl chamber 6 in. diam. and $6\frac{1}{2}$ in. long provided with tangential inlets and outlets. The cover of one end was a 'push on' fit and blew off when back firing through the carburetor (induction ignition) occurred.

The Inlet Valve.—The standard inlet valve is fitted with a 180° shroud so arranged that the combustible mixture is given a swirling motion on entering the cylinder. The arrangement has been found of beneficial effect in respect of determinations of the relative antiknock values of gasolines, but it reduces volumetric efficiency and is not used in practice.

Definition of the Terms Used to Describe Abnormal Ignition or Combustion

Detonation knock describes an effect due to the self-ignition and explosion of the gas ahead of the flame (end gas). Eliminating the knock by retarding ignition gives rise to a *decrease* of power.

Combustion knock describes an effect due to an abnormally high rate of flame propagation. The knocking sound in the C.F.R. engine is similar to that heard when detonation occurs. Eliminating or reducing the knock by retarding ignition gives rise to an *increase* of power. This characteristic makes it possible to distinguish between combustion knock and detonation knock.

Induction ignition describes the effect obtained when the combustible mixture ignites before the inlet valve closes. The effect gives rise to explosions in the induction system and carburetor, the violence depending on mixture proportion and the volume involved. The explosions occur irregularly.

Pre-ignition is initiation of combustion after the inlet valve closes and before ignition by spark. If the ignition occurs sufficiently late in the compression stroke, the engine will run without spark ignition but generally at reduced power and for relatively short periods of time.

Preliminary Engine Experiments with Unclean Combustion Chamber

The experiments were begun with the engine as found. It had been run for some weeks on hydrocarbon fuels, generally leaded. The compression ratio was set at 5 : 1, the ignition timing at 30° advance, and the engine run at 900 r.p.m. for a warming up period of one hour on leaded gasoline. The gasoline was then shut off* and hydrogen admitted at a sufficient rate to maintain the engine speed of 900 r.p.m., with light load. On increasing the rate of hydrogen supply and the load, severe knocking occurred, accompanied by occasional induction ignition. Thus the characteristics of hydrogen combustion in an engine as observed by Ricardo, Burstall, and Egerton had been recovered.

Very rich mixtures were then admitted. Combustion was silent and without induction ignition, just as when very weak mixtures were used. This interesting characteristic seems to have been overlooked by earlier experimenters.

It was observed during the experiments mentioned that knock always decreased on retarding ignition, while power increased; this indicated combustion knock rather than detonation knock.

The engine was dismantled for observation of the condition of the combustion chamber surfaces. The piston crown was found to be thickly coated with hard carbon. The piston ring grooves contained granular carbon but the rings were free. The exhaust valve was coated with a greyish white deposit. The inlet valve was fairly clean. The surfaces were thoroughly cleaned and the shrouded inlet valve replaced by a spare exhaust valve of the common tulip shaped type.

First Set of Trials with the Engine Combustion Space Initially Clean. Jacket Temperature, 212° F.; Compression Ratios Rising to 10 : 1, and Arbitrarily Chosen Ignition Timing

Preliminary trials were carried out after warming up the engine by running on leaded gasoline before changing over to hydrogen. There was then no induction ignition at any compression ratio within the range of the engine. Combustion was silent at compression ratios up to 8 : 1 but slight combustion knock occurred at 10 : 1 when using the mixture strength for maximum power. It developed later that ignition had been set too far advanced.

A complete set of trials was then carried out at compression ratios of 4.2, 6.0, 8.0, and 10 : 1 and with the hydrogen-air mixtures varying from very weak to very rich. It was supposed, judging from experiments made by others, that a considerable spark advance would be required for weak mixtures used at low compression ratios and less advance on increasing mixture strength and compression ratio, but nothing definite was known because previously it had not been possible to use anything but weak mixtures at any compression ratio. Trial spark settings of 30°, 20°, 10°, and 0° for the compression ratios mentioned were therefore used.

* The engine was warmed up by running on gasoline in order to save hydrogen.

The experimental results are given by the graphs of Fig. 1; net power output in kilowatts being plotted against rate of hydrogen supply. The values for rate of hydrogen supply are the square roots of pressure differences in inches

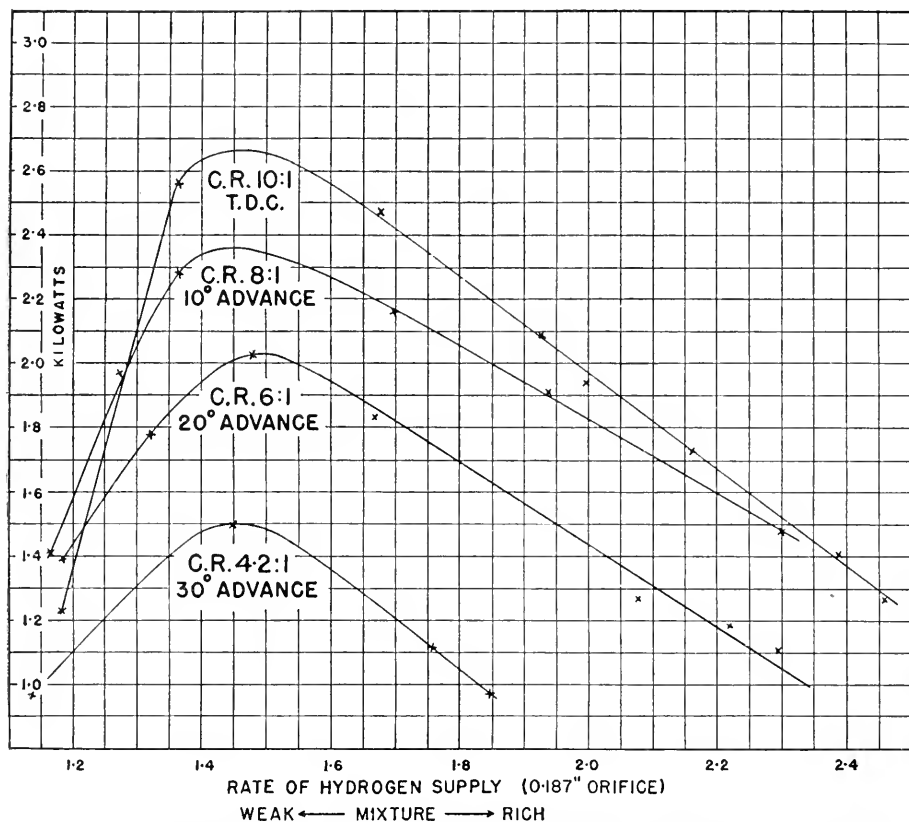


FIG. 1. Relation between power output and mixture strength at compression ratios rising to 10 : 1. Jacket temperature, 212° F.

of water across a circular square edged metering orifice, 0.187 in. diameter, in a thin plate. The graphs are of interest in showing for the first time on record that it is possible to run an engine on hydrogen in any proportion in a mixture with air at compression ratios rising to 10 : 1 and without any combustion difficulty as is evidenced by the consistent variations of power with changes of compression ratio and mixture strength.

Sundry Experiments and Recurrence of Induction Ignition and Knock

Air oscillation in the induction system of the C.F.R. engine is considerable and it appeared that some of the hydrogen supplied at the carburetor throat might accordingly be carried out of the standard inlet pipe to escape into the atmosphere. The standard pipe was therefore replaced by the swirl chamber.

The 0.187 in. diam. orifice for metering the hydrogen was replaced by one of 0.125 in. diam. in order to obtain greater and more easily readable pressure differences, and for further convenience of reading pressure differences the U-tube type of manometer was replaced by one of the single leg variety.

Experiments with hydrogen were resumed on completion of the changes mentioned, after the usual warming up of the engine by running for an hour on leaded gasoline. The earlier combustion difficulties were again encountered and it was impossible to run with the 'correct' mixture strength, even at the low compression ratio of 4 : 1, without violent explosions in the induction system. The difficulties were not overcome by replacing the swirl chamber by the standard inlet pipe, by warming up the engine on unleaded gasoline, or by approaching 'correct' mixture strength from the rich instead of the weak side, or by lowering or raising the jacket temperature, or by taking precautions to avoid electric charges in the induction system possibly due to the high velocity of the mixture passing over sharp edges.

The time of running since the first cleaning was about 12 hr. and the engine was dismantled for inspection of the combustion space and the valves. Both valves were found to have been seating properly and were clean. The exhaust valve showed oxidation colors, brown and red. The piston rings were free but there was some loose carbon in the grooves. The water cooled surfaces were free of loose carbon. The significant finding was a layer of *fluffy carbon*, having the appearance of lamp black, on the piston crown. The combustion chamber, the inlet passageways, and the ring grooves were thoroughly cleaned and the engine reassembled for further trials.

Second Set of Trials, Combustion Space again Initially Clean. Jacket Temperature, 212° F. Air Supply Through Swirl Chamber with Cover Off

The trials were made primarily to verify that the recurrence of combustion difficulties was due to the fluffy carbon mentioned above. They were run at compression ratios of 6, 8, and 10 : 1 and spark setting varied to determine optimum values in varying conditions of mixture strength and compression ratio. There was not a single case of induction ignition in the whole set of trials; combustion was notably quiet except when using the mixture strength for maximum power at a compression ratio of 10 : 1. There was then slight combustion knock.

The experimental results are given by the three sets of graphs of Fig. 2. It is of special interest that maximum power for any but the weakest or richest mixture was obtained when ignition occurred at or very near top dead center. At 10 : 1 compression ratio maximum power was obtained with the spark 5° *retarded*. Regular ignition at this high compression ratio was obtained by reducing the spark gap from the standard setting of 0.025 in. to 0.013 in. Maximum power at 8 : 1 compression ratio was obtained with a spark advance of 5°, whereas at the lower compression ratio of 6 : 1, the optimum setting was at 0°, a somewhat inconsistent result justifying a repetition of the experiments.

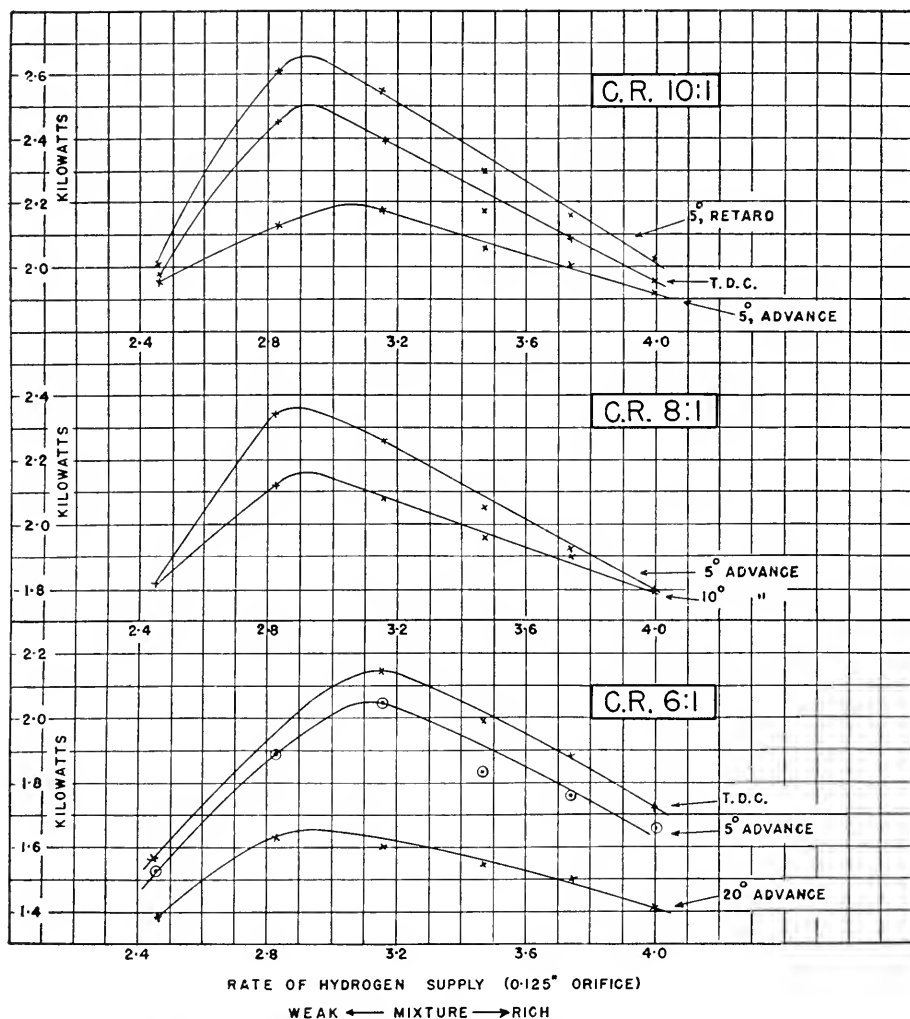


FIG. 2. The effect of ignition timing on power output at compression ratios rising to 10 : 1. Jacket temperature, 212° F.

Routine Cleaning Method

The experiments described above occupied about two hours' running time and no doubt the usual combustion difficulties would have recurred on continued running if no precaution had been taken to maintain the combustion space reasonably clear of fluffy carbon. A routine cleaning method was therefore adopted. Thus, always before starting a day's experiments the bouncing pin and spark plug were removed, the piston moved to top dead center, and the crown cleaned with a tooth brush inserted through the spark plug hole. The engine was then motored round to blow loose carbon through the holes mentioned. As a further precaution to avoid carbon formation by

pyrolysis of hydrocarbon fuel the warming up period on gasoline was reduced to the time required to heat the jacket water to the boiling point and any further warming up done with hydrogen.

The engine was used after the adoption of the cleaning routine for a complete set of trials at low jacket temperature, extended trials using town gas and some sundry experiments made in preparation for future experimental work. There was no recurrence of combustion difficulties.

Third Set of Trials, Routine Cleaning of Combustion Space. Jacket Temperature, 95° to 100° F.

The experiments so far described were made with the standard C.F.R. method of evaporative cooling of the water jackets, that is, jacket water temperature was always 212° F. It is not customary to use such high temperatures in practice and as a matter of interest a set of trials was made with the jackets cooled by tap water, the flow being regulated to maintain an outlet temperature of 95° to 100° F. The standard C.F.R. air inlet pipe was used because it was found during the sundry trials mentioned above that slightly more power was obtained than when using the swirl chamber inlet, no doubt because of the ramming effect of the pipe.

The optimum spark setting for compression ratios of 4, 6, 8, and 10 : 1 was determined for varying mixture strengths. It was found that the optimum setting for the maximum power mixture strength was also the optimum for any richer mixture. But for mixtures on the weak side there would be some advantage in advancing the ignition progressively in accordance with the diminution of hydrogen concentration in the mixture with air.

The trials were made when using the optimum spark setting for the maximum power mixture strength. The experimental results are given by the graphs of Fig. 3. The running of the engine was exceptionally smooth and quiet even when using the mixture strength for maximum power at a compression ratio of 10 : 1.

It will be noted that the graphs are nearly parallel on the rich mixture side but not on the weak side, as would be expected from the finding that the optimum spark advance for the maximum power mixture was also the optimum for richer but not for weaker mixtures.

The Effect of Carbon Nuclei Added to the Hydrogen-Air Mixture

It has been demonstrated by the experiments so far described that induction ignition and combustion knock in the hydrogen engine are due to the igniting action of carbon nuclei derived from the pyrolysis of the lubricating oil. It became of interest, therefore, to observe the effect of carbon nuclei added to the entering gaseous mixture.

The carbon used for the experiments was pulverized charcoal screened with a 200 mesh sieve. It was described as having been activated by heating but had been standing open to the laboratory atmosphere for some weeks before

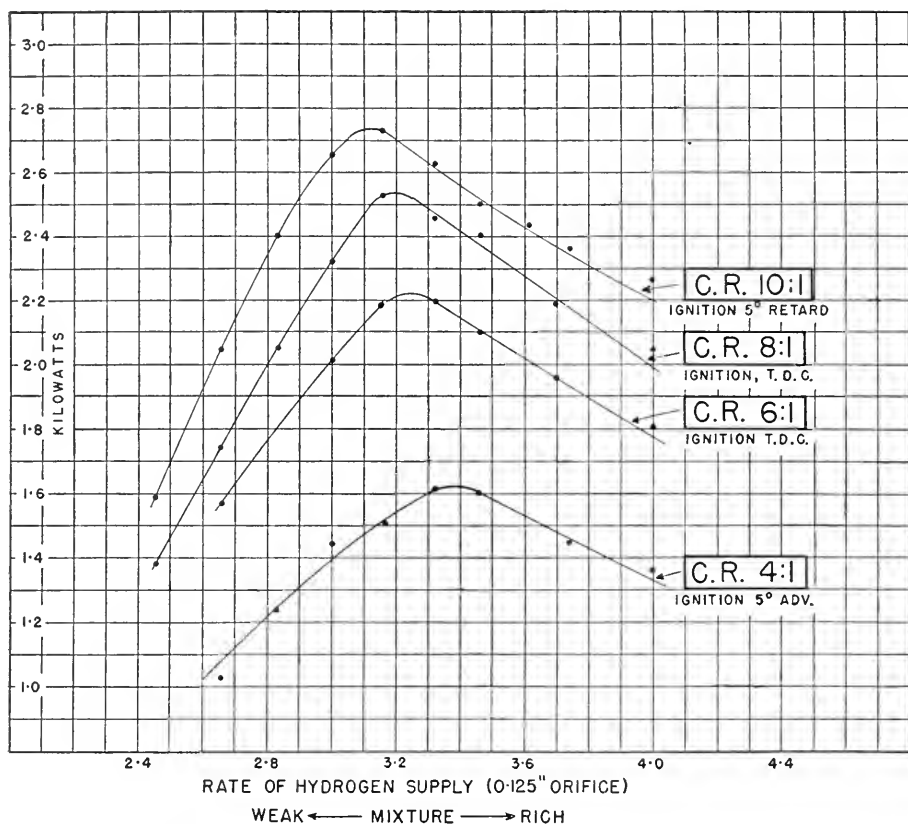


FIG. 3. Relation between power output and mixture strength at compression ratios rising to 10 : 1, nearly optimum ignition timing. Jacket temperature, 95 to 100° F.

being used for the experiments. The carbon was admitted to the air stream in advance of the carburetor throat, at a measured rate, by a device similar to a screw feed coal stoker. The experiment was begun with the combustion space in the condition maintained by the routine cleaning method. The standard pipe inlet was fitted and the jacket water maintained at 212° F. by the standard method.

The engine was started on hydrogen and run at a compression ratio of 6 : 1, with the mixture strength for maximum power and ignition at top dead center. There was no induction ignition, and combustion was silent. The carbon was then admitted at a rate of approximately 2.0 mgm. per stroke. Combustion knock occurred almost immediately and was followed by induction ignition accompanied by explosions in the induction system.

Preparations had been made to carry out a series of experiments to measure the rate of carbon supply required to induce premature ignition and combustion knock or detonation at compression ratios rising to 10 : 1, but, perhaps

as should have been expected, the carbon dust accumulated in the engine to such an extent that induction ignition and combustion knock continued when the supply of carbon to the induction system was shut off.

Indicated Mean Effective Pressure and Indicated Thermal Efficiency

The experiments with the hydrogen engine are regarded as confirming the nuclear theory of ignition. It is of importance, nevertheless, to show that confirmation was obtained while values of the indicated mean effective pressure (I.M.E.P.) and indicated thermal efficiency were such as would be expected from the compression ratios and mixture strengths used during the experiments.

The indicated power was determined by the motoring method. That is, the power required to motor the engine at the experimental speed of 900 r.p.m. was measured immediately after cutting off the fuel supply and added to the net power output measured previously. The method has been widely used by Ricardo and others, and, although it involves the unwarranted assumption that engine friction is of the fluid variety and therefore independent of load, values obtained accordingly are useful for purposes of comparison.

I.M.E.P.—The power required to motor the engine at 900 r.p.m., jacket temperature 212° F., was determined after warming up, using benzene as the fuel, at compression ratios of 6, 8, and 10 : 1. The piston area is 8.28 sq. in., stroke 0.375 ft., and at 900 r.p.m.—

$$\text{I.M.E.P. (lb. per sq. in.)} = \text{Indicated horse power} \times 23.6.$$

Maximum power output being taken from the graphs of Fig. 2, the data given in Table I are obtained.

TABLE I

INDICATED MEAN EFFECTIVE PRESSURES AT COMPRESSION RATIOS OF 6, 8, AND 10 : 1,
WHEN USING THE MAXIMUM POWER MIXTURE STRENGTH

Compression ratio	Net output, kw.	Motoring power, kw.	I.H.P.	I.M.E.P., lb./sq. in.
10 : 1	2.66	1.61	5.73	136
8 : 1	2.36	1.59	5.30	125
6 : 1	2.15	1.48	4.87	103

Indicated Thermal Efficiency.—Relative rates of hydrogen supply are reasonably accurate but approximate values only of quantities were obtained, the metering orifice not having been calibrated. Thermal efficiencies calculated accordingly, again using data from Fig. 2, are given in Table II.

TABLE II
INDICATED THERMAL EFFICIENCIES; COMPRESSION RATIO, 10 : 1

Mixture strength	Net power, kw.	Indicated power, kw.	I.H.P.	Indicated thermal efficiency, %
15% rich	2.40	4.01	5.38	34.2
3% rich	2.64	4.25	5.70	39.8
Max. power	2.66	4.27	5.78	41.2
5% weak	2.58	4.19	5.62	42.4
17% weak	2.02	3.63	4.87	42.0

It will be noted from Table II that maximum efficiency was obtained for the mixture strength giving somewhat less than maximum power, as would be expected.

Section II

Discussion of Experimental Results

Induction ignition, normally described as "firing back through the carburetor", was obtained when, starting with a clean engine, sufficient time elapsed for an accumulation of fluffy carbon in the combustion space. The effect was not obtained if accumulation of the carbon were prevented. It is concluded that ignition of the fresh charge when obtained was due to glowing particles of carbon present in the residual charge.

Ignition by sudden compression.—The absence of the effect when the engine combustion space was nearly free of fluffy carbon is of interest in respect of experiments by others on the ignition of electrolytic gas ($2\text{H}_2 + \text{O}_2$) and hydrogen-air mixtures by sudden compression. Falk (5,6) concluded that the presence of lubricant (lanoline) was without effect on ignition temperature, but the experiments of Dixon, Bradshaw, and Campbell (2) and Dixon and Crofts (3) demonstrated that consistent ignition temperatures could be obtained solely when the lubricant was present as an extremely thin film on the surface of the combustion space, a condition set by the vacuum method of filling the space with the combustible mixture. Tizard (14), using the Ricardo compression ignition machine, similar to an engine cylinder, could not avoid the presence of a thin film of lubricant on surfaces exposed to the temperatures of compression and obtained ignition temperatures accordingly. When the Ricardo machine was redesigned to permit compression of the combustible mixture in a cylinder supposed to be free of lubricant, Tizard and Pye (15) were unable to obtain consistent ignition temperatures. Fenning (8), on continuing experiments with the machine, found that lubricant did in fact penetrate into the compression cylinder in an irregular manner. Thus, out of five compressions with a compression ratio of 9.2 : 1 and a jacket temperature of 97°C ., two compressions resulted in premature ignition, two caused ignition after delay periods of 0.009 and 0.015 sec. and a fifth failed to cause ignition.

Nevertheless, when using the hydrogen engine at 10 : 1 compression ratio, a jacket temperature of 100° C. and more nearly adiabatic compression, the mixture failed to ignite prior to passage of the spark, if the combustion space were nearly free of finely divided carbon. That is, ignition did not occur in the body of the gaseous mixture in the absence of material nuclei of ignition as would be expected from the experiments of King (9) and King and Mole (11).

Flame velocity.—It is generally agreed that maximum engine power is obtained when maximum combustion pressure occurs about 12° after top dead center. It will be seen from Figs. 2 and 3 that at 10 : 1 compression ratio maximum power was obtained when the spark passed at 5° after top dead center. Combustion was thus completed in about 7° of crank angle, that is in 0.0013 sec., engine speed being 900 r.p.m. The flame would have traveled a distance equal to the diameter of the cylinder, 3.25 in., so velocity must have been approximately 63 m. per sec. even with no allowance for the time interval between passing the spark and the start of pressure rise. Flame velocity in the nearly clean combustion space of the engine is comparable with that observed by Fenning (7) when similar mixtures in a clean bomb were ignited by a spark, if allowance be made for differences in dimensions, initial temperature, and pressure. The flame velocity attained in the engine or bomb did not approach that of true detonation and in neither case was there any evidence of that phenomenon.

The pro-knock effect of carbon nuclei.—When hydrocarbon fuels, especially paraffins, are used in an engine, finely divided carbon can be derived from pyrolysis of the fuel, and maximum concentration occurs necessarily in the end gas [Part IV (10)]. Self-ignition can occur accordingly and nearly simultaneously throughout the mass of the gas; this results in detonation knock.

When hydrogen is used as the fuel, finely divided carbon can be obtained from the lubricating oil only and must be distributed by turbulence, more or less uniformly. There can be no preferential concentration in the end gas, consequently the sole effect of the carbon, after the passage of the spark, is to increase flame velocity and thereby promote combustion knock, an effect similar to that obtained by Fenning (7) on igniting electrolytic gas when the time from the passage of the spark to the attainment of maximum pressure was as short as 0.00072 sec., that is, combustion knock was obtained in the bomb on increasing flame speed by using electrolytic gas and in the engine by impregnating hydrogen-air mixtures with finely divided carbon.

Acknowledgments

The experimental work described in this paper was made possible by the interest of Prof. E. A. Allcut, Head of the Department of Mechanical Engineering, University of Toronto, in the nuclear theory of ignition and by a Grant-in-Aid from the Defence Research Board (Canada).

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THE OXIDATION, IGNITION, AND DETONATION OF
FUEL VAPORS AND GASES

VI. THE PREVENTION OF PRE-IGNITION AND DETONATION
IN GAS ENGINES

By R. O. KING, W. A. WALLACE AND B. MAHAPATRA

THE OXIDATION, IGNITION, AND DETONATION OF FUEL VAPORS AND GASES

VI. THE PREVENTION OF PRE-IGNITION AND DETONATION IN GAS ENGINES¹

By R. O. KING², W. A. WALLACE³ AND B. MAHAPATRA⁴

Abstract

The experiments described show that town gas containing hydrogen in large concentration can be used as fuel for a carburetor type Otto cycle engine at compression ratios rising to 10 : 1 and in mixtures with air in any proportion, if the accumulation of fluffy carbon in the combustion space be prevented. The carbon is produced mainly by pyrolysis of the lubricating oil. Confirmation of the nuclear theory of ignition, advanced in Part IV to explain the cause of detonation in engines, is thus obtained. Performance data are given for the variation of power and economy with mixture strength and ignition timing at compression ratios of 6, 8, and 10 : 1.

Introduction

It has long been known that the power and efficiency of gas engines have been limited by the necessity of using relatively weak gas-air mixtures and low compression ratios in order to avoid pre-ignition and detonation. Both effects are commonly believed to be due to ignition of the combustible mixture by sudden compression and/or by hot surfaces in the combustion space. Both increase in severity with increase in the proportion of hydrogen in the gas.

The severity of the effects mentioned has been mitigated by reducing the inflammability of the combustible mixture or by cooling the more highly heated surfaces of the combustion space. Thus, Dugald Clerk (1) added cooled exhaust gases to the entering mixture; Bertram Hopkinson (4) provided a water sprinkler system in the combustion space and a modification of the system was used in the Crossley Gas Engine (2, p. 39). The Koerting Gas Engine (German) was fitted with a separate water cooled body in the combustion space (2, p. 95). Recent developments aimed to avoid pre-ignition and detonation are the high compression gas engine and the Dual Fuel engine using gas and injected oil. Both operate at Diesel engine compression ratios. High pressure gas is injected late in the compression stroke in the first mentioned type (Walter (9) and Erren (3)) and ignition is by electric spark. Ignition is by injected oil in the Dual Fuel type as in the compression ignition engine, and mixing of the gas with air does not occur until the inlet valve opens (Jones (5, p. 37)).

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Contribution by the Defence Research Board (Canada) and the Department of Mechanical Engineering, University of Toronto.

² Research Scientist, Naval Division, Defence Research Board. Special Lecturer, Mechanical Engineering, University of Toronto, lately Director of Scientific Research and Development, Royal Canadian Navy.

³ Lecturer in the Department of Mechanical Engineering, University of Toronto.

⁴ Overseas Scholar, Government of India.

The above mentioned methods of increasing the power and economy of gas engines are based on the theory that pre-ignition and detonation are inherent in the nature of the gas, especially of the hydrogen constituent. It is shown, however, by the experiments described in Part V (8) that the pre-ignition and detonation observed when hydrogen-air mixtures are used in an engine are due to the igniting effect of finely divided carbon derived from pyrolysis of the lubricating oil.

Commercial fuel gases, even if composed mainly of hydrogen and carbon monoxide, usually contain some proportion of hydrocarbon which by pyrolysis at end gas temperatures might yield finely divided carbon in sufficient concentration to cause ignition and consequent detonation (Part IV (7)). The lubricating oil would otherwise be the sole source of carbon, as when using hydrogen.

It became of interest, therefore, to determine if pre-ignition and detonation in engines using fuel gas could be avoided, as in the hydrogen engine, by preventing the accumulation of finely divided carbon in the combustion space. Experiments made accordingly are described in this Part and show that the gas, pre-mixed with air in any proportion, can be used at compression ratios rising to 10 : 1, the limit of the variable compression C.F.R. engine, without pre-ignition or detonation and with a consequent increase in power and economy.

Experimental

The C.F.R. knock testing engine in the Department of Mechanical Engineering, University of Toronto, was used for the experiments with Toronto town gas as the fuel. The special features of the engine are described in Part V (8).

The Fuel Gas

The composition and calorific value of Toronto town gas are checked continuously by the Consumers Gas Company. The composition at the time of the experiments was as below, in percentage volumes.

Hydrogen	49.1	Ethane	2.3
Carbon monoxide	19.1	Nitrogen	7.8
Methane	12.9	Carbon dioxide	3.7
Heavy hydrocarbons	4.3	Oxygen	0.8

The calorific value was 475 B.t.u. per cu. ft. at 60° F. and 30 in. of mercury barometric pressure, when saturated with water vapor. Temperature at time of use was 78.5° F. and pressure 29.9 in. of mercury, the calorific value being then,—

$$475 \times \frac{520}{538.5} \times \frac{29.9}{30} = 459 \text{ B.t.u.}$$

The gas was supplied to the engine by using the device illustrated in Fig. 1, the standard diffuser being removed from the throat of the carburetor venturi.

The C.F.R. carburetor was otherwise intact and a change to liquid fuel could be made when required.

The rate of gas supply to the engine was measured by a new and freshly calibrated No. 1A Sprague meter.

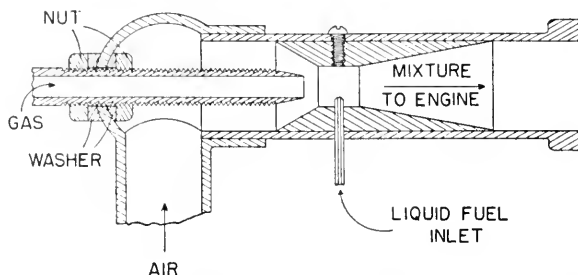


FIG. 1. Carburetor arrangement used for running the C.F.R. engine on town gas.

Experimental Procedure and Conditions

The engine had been run on hydrogen prior to the experiments with town gas and the routine cleaning method then adopted, Part V (8), to prevent the accumulation of fluffy carbon in the combustion space was continued. The engine was always run at 900 r.p.m. The jacket water temperature was maintained at 212° F. by the C.F.R. standard method of evaporative cooling, using distilled water.

The rate of flame propagation in town gas – air mixtures is so much slower than in hydrogen–air mixtures and varies so much with mixture strength that maximum power for a particular compression ratio and mixture strength is obtained only if a particular ignition timing is used. It was decided, therefore, to run series of experiments at compression ratios of 6, 8, and 10 : 1 to determine the ignition timing required for maximum power when using a series of mixture strengths varying from very weak to very rich. Families of graphs were thus obtained relating maximum power to ignition timing and mixture strength at the three values of the compression ratio.

Experimental Results

The combined effect of mixture strength and ignition timing on power output when the compression ratio was 6 : 1 is shown by the graphs of Fig. 2. Similar families of graphs were obtained for compression ratios of 8 and 10 : 1, but are not reproduced.

The graphs of Fig. 3 then give the relation between power output and mixture strength when the optimum ignition timing is used for every experimental point; the timing in degrees advance being given by the figures in circles.

The engine ran smoothly without combustion noise even at the maximum available compression ratio of 10 : 1, and when using the mixture strength and spark advance giving maximum power.

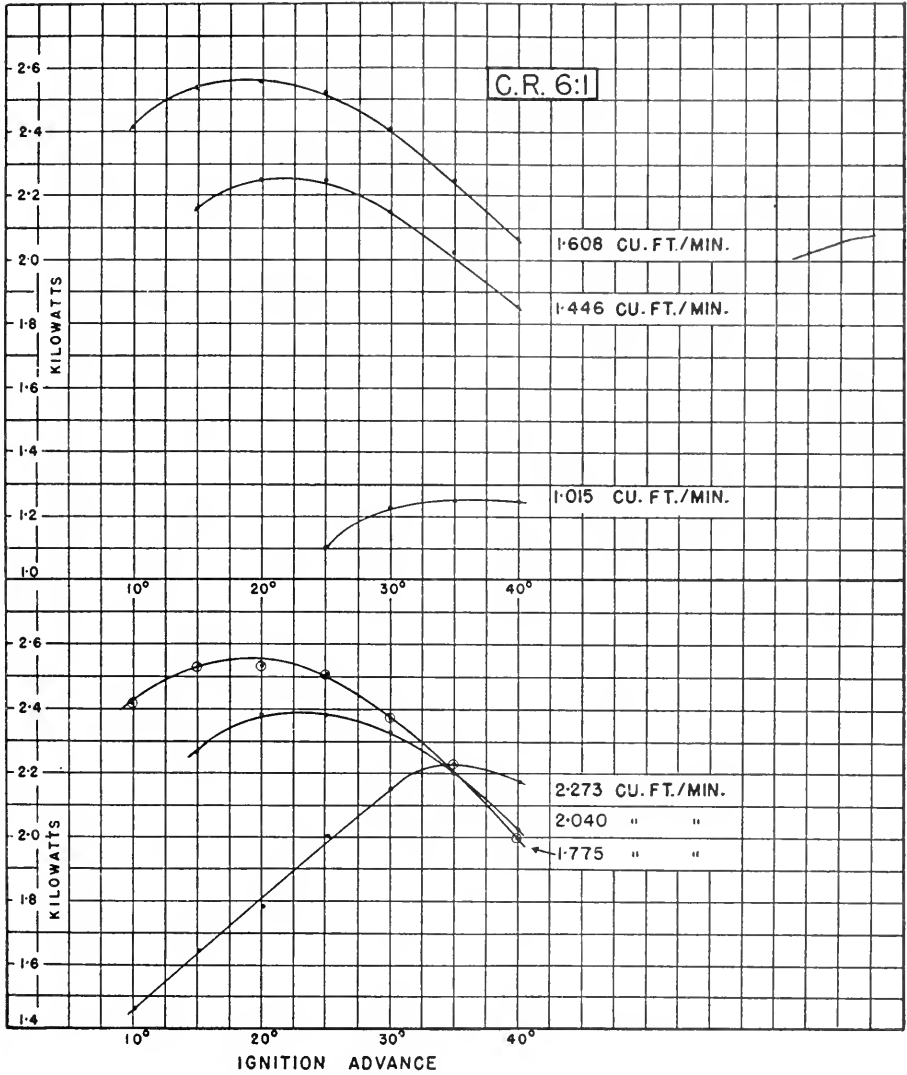


FIG. 2. Effect of mixture strength and ignition advance on power output when using town gas as fuel for the C.F.R. engine, running at 900 r.p.m., compression ratio 6 : 1.

Indicated thermal efficiencies and indicated mean effective pressures calculated from the graphs of Fig. 3 are given in Tables I, II, and III for compression ratios of 6, 8, and 10 : 1, respectively, and for varying mixture strengths. The percentages of mixture strength are in respect of the rate of gas supply required for maximum power, and it will be seen by reference to the graphs of Fig. 3 that this rate varies with compression ratio.

The values for indicated horse power given in the tables were obtained by the usual motor method. The power loss obtained accordingly is added to the net power output. The losses in the C.F.R. unit used for the experiments

are large because they include the electrical and mechanical losses in both the main and auxiliary generators in addition to the pumping and mechanical losses in the engine which could not be measured separately because the engine

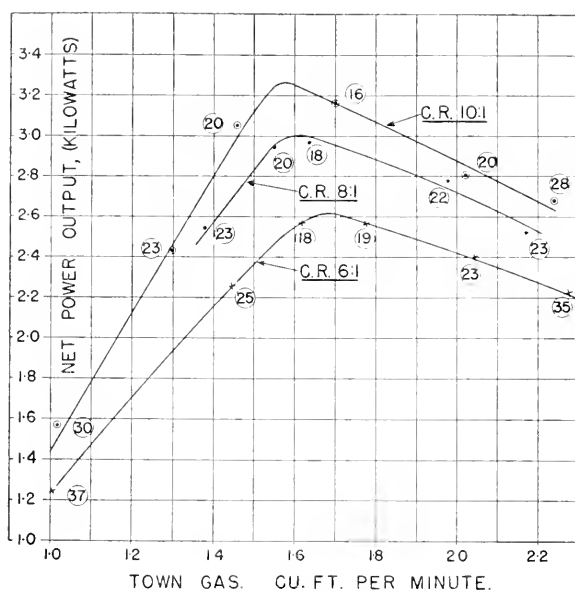


FIG. 3. Relation between power output and mixture strength at compression ratios of 6, 8, and 10 : 1, with optimum ignition advance as shown by figures in circles, C.F.R. engine running on town gas at 900 r.p.m.

TABLE I
COMPRESSION RATIO 6 : 1

Gas - air mixture	Cu. ft. gas/min.	I.H.P.	Indicated thermal efficiency	I.M.E.P., lb./sq. in.
30% weak	1.17	4.20	0.33	98
20% weak	1.34	4.70	0.32½	110
10% weak	1.51	5.19	0.32	121
Max. power	1.68	5.51	0.30	129
10% rich	1.85	5.37	0.28	126
20% rich	2.02	5.24	0.25	122
30% rich	2.18	5.05	0.22	118

was not fitted with a swinging field electrical dynamometer. The total losses measured after the engine had been raised to working temperature by running on benzene were, in kilowatts, 1.61 at 10 : 1 C.R.; 1.59 at 8 : 1 C.R.; 1.48 at 6 : 1 C.R.

The cylinder diameter of the engine is 3.25 in., the stroke is 4.5 in. and as the trials were run at 900 r.p.m., indicated mean effective pressure (I.M.E.P.) in pounds per square inch,

$$= \text{Indicated horsepower} \times 23.41 .$$

TABLE II
COMPRESSION RATIO 8 : 1

Gas - air mixture	Cu. ft. gas/min.	I.H.P.	Indicated thermal efficiency	I.M.E.P., lb./sq. in.
15% weak	1.37	5.48	0.37	128
10% weak	1.50	5.94	0.37	139
Max. power	1.61	6.15	0.36	144
10% rich	1.77	6.02	0.32	141
20% rich	1.93	5.86	0.28	137
30% rich	2.09	5.67	0.25	133

TABLE III
COMPRESSION RATIO 10 : 1

Gas - air mixture	Cu. ft. gas/min.	I.H.P.	Indicated thermal efficiency	I.M.E.P., lb./sq. in.
30% weak	1.10	4.54	0.38	106
20% weak	1.25	5.24	0.39	122
10% weak	1.41	5.95	0.39	139
Max. power	1.57	6.53	0.38	153
10% rich	1.73	6.36	0.34	149
20% rich	1.88	6.18	0.30	145
30% rich	2.04	5.96	0.27	139

Taking the calorific value* of the gas in British thermal units and using f.p.s. units, the indicated thermal efficiency,

$$= \frac{\text{Indicated hp.} \times 33000}{\text{Cu. ft. gas per min.} \times \text{calorific value} \times 778}$$

Discussion of Experimental Results

The primary object of the experiments was to test the validity of the nuclear theory of ignition advanced in Part IV (7) as a working hypothesis for investigations of combustion as it occurs in engines. The results confirm the theory in that ignition of town gas-air mixtures was not obtained by nearly adiabatic compression in a combustion space maintained at 212° F. and containing a hot exhaust valve, compression ratio being 10 : 1, if the concentration of nuclei of ignition, as finely divided carbon, was maintained at a relatively low value.

The experiments considered as engine trials to determine power and efficiency are regarded as of a preliminary nature. Measurements were, however, made with the degree of accuracy usually employed in engine trials and the values obtained for indicated thermal efficiency and indicated mean effective pressure, as given in Tables I, II, and III, are of interest.

* The "higher" calorific value of 459 B.t.u. per cubic foot was used in the calculations.

Indicated Thermal Efficiency

It is generally considered that thermal efficiency increases substantially on going to weak mixtures. This characteristic is shown by the increase of 10% for 6 : 1 compression ratio, Table I, but referring to Tables II and III it will be noted that thermal efficiency tends to become constant on the weak side of maximum power mixture strength, as the compression ratio is increased; furthermore the mixture strength required for maximum power diminishes appreciably as the compression ratio is raised. Both effects may be due to the ignition advance for maximum power at any mixture strength, diminishing as compression ratio is raised as shown by the figures in circles, Fig. 3. Heat of combustion would be added more nearly at constant volume with decrease in ignition advance, and, the combustion period being shortened accordingly, less heat would be lost to the cool surfaces of the combustion chamber. Thus when hydrogen was used in the engine and ignition advance was zero or even -5° , the maximum thermal efficiency obtained, Part V (8), was 0.42 as compared with 0.39 for town gas, or 70% and 65%, respectively, of the air standard efficiency of 0.598 at 10 : 1 compression ratio.

Mean Effective Pressure

A maximum of 153 lb. per sq. in. was obtained for indicated mean effective pressure at 10 : 1 compression ratio (see Table III). The mechanical efficiency of the C.F.R. engine used for the experiments could not be measured but is known to vary from 85% to 88% in engines of the type. Assuming the lower value, 130 lb. per sq. in. is obtained for the brake mean effective pressure. According to Kent (6, p. 1236) it is necessary to limit B.M.E.P. in ordinary gas engines to 65 lb. per sq. in. to avoid pre-ignition and detonation, especially when using coke oven or illuminating gas; both these gases and Toronto town gas contain hydrogen in similar large proportion. The limitation has been shown to be unnecessary if nuclear ignition be avoided, and it is of interest to compare the performance of the C.F.R. engine obtained accordingly with that of the 'National' gas engine in the Heat Engine Laboratory, University of Toronto. The relevant data are given in Table IV.

TABLE IV

FULL POWER PERFORMANCE DATA, C.F.R. AND 'NATIONAL' GAS ENGINES, ON TOWN GAS

Engine	R.p.m.	Gas per I.H.P./hr., cu. ft.	Compression ratio	I.M.E.P., lb./sq. in.	Indicated thermal efficiency
C.F.R.	900	14.4	10 : 1	153	0.38
National	180	18.9	4.85 : 1	95	0.28

The higher mean effective pressure and speed of the C.F.R. have a favorable effect on power-to-weight ratio. Thus, I.H.P. of the C.F.R. is 17.5 per 100 cu. in. of piston displacement, whereas the similar figure for the National engine is 2.17 only.

Conclusion

The experiments show that on preventing nuclear ignition of the gas-air mixture it becomes possible to operate the C.F.R. engine at any desired compression ratio while using mixture strengths varying from very weak to very rich and to obtain corresponding power and economy. The engine was run without throttle control, and, by using a relatively high compression ratio, 10 : 1 for example, power output could be varied over a wide range by controlling the rate of gas supply.

Acknowledgments

The experimental work was made possible by the interest of Prof. E. A. Allcut, Head of the Department of Mechanical Engineering, University of Toronto, in the nuclear theory of ignition and by a Grant-in-Aid from the Defence Research Board (Canada). The willing co-operation of the Consumers Gas Company of Toronto, represented by Mr. J. A. Morrison, was greatly appreciated.

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**THE OXIDATION, IGNITION, AND DETONATION OF
FUEL VAPORS AND GASES**

**VII. THE OXIDATION OF PENTANE IN VARYING CONCENTRATION IN AIR
AT TEMPERATURES RISING TO 700° C. AND THE EFFECT
OF IRON CARBONYL ON REACTION VELOCITY**

By R. O. KING

THE OXIDATION, IGNITION, AND DETONATION OF FUEL VAPORS AND GASES

VII. THE OXIDATION OF PENTANE IN VARYING CONCENTRATION IN AIR AT TEMPERATURES RISING TO 700° C. AND THE EFFECT OF IRON CARBONYL ON REACTION VELOCITY¹

BY R. O. KING²

Abstract

Results are given for the oxidation in reaction chamber No. 10 of pentane mixed with air, mixture strength being varied from 25% weak to 100% rich. Oxidations were carried out with and without additions of iron carbonyl to the pentane. The experiments were made mainly to find a rational explanation for the antiknock property of rich fuel-air mixtures. The experimental results for undoped mixtures show that, at temperatures approaching those of the end gas in an engine, reaction velocity increases by 100% on increasing mixture strength over the range mentioned above and by 100% on increasing temperature from 600° to 650° C. Similar increases in reaction velocity with rise of temperature and with increase of mixture strength were obtained for the doped mixtures over the high temperature range but at temperatures 150° C. lower than for undoped mixtures. The characteristics of the experimental results confirm the conclusion reached in earlier Parts, namely, that oxidation of pentane in the conditions of the experiments is a heterogeneous reaction.

Introduction

It has been shown by experiments already described (1, 2, 3) that oxidations of pentane and hexane can be carried out in reaction chamber No. 10, without explosion, at whatever temperature may be required for completion of reaction. The experiments, with one exception, were made when using mixtures of combining proportions with air. Their oxidation characteristics are described in the references quoted and experimental evidence given showing that detonation in an engine is delayed or prevented by dilution of the end gas with oxidation products (3).

The liability of a fuel-air mixture to detonate varies with mixture strength, and the experiments to be described in this Part were made to determine the oxidation characteristics of weak and rich mixtures, in particular to ascertain the fundamental reason for the antiknock property of rich mixtures which is of importance in practice.

Experimental Arrangements

The No. 10 reaction chamber used for the experiments was of Jena Supramax glass and of the dimensions given in Part I (1). Pentane, taken as before, as a representative liquid paraffin hydrocarbon was used to form mixtures with air in varying proportions. The pentane and the methods of measurement were as described in the appendix to Part I.

¹ Manuscript received May 28, 1948.

Contribution from Defence Research Board, Ottawa, Canada.

² Research Scientist, Naval Division, Defence Research Board, lately Director of Scientific Research and Development, Royal Canadian Navy.

The rate of air supply to the reaction chamber in cubic centimeters per minute was measured at room temperature and the pentane added as liquid in conditions ensuring that vaporization was complete before the mixture entered the chamber.

A pentane-air mixture is defined as being weak or rich according to the percentage by which the pentane constituent is less or greater than that required for combining proportions.

Thus,—

Combining proportions mixture is	$C_5H_{12} + 8 O_2 + 30.3 N_2$
100% rich mixture is	$2C_5H_{12} + 8 O_2 + 30.3 N_2$
25% weak mixture is	$0.75C_5H_{12} + 8 O_2 + 30.3 N_2$

A combining proportions mixture of pentane with air would, according to kinetic theory, contain 2.87% only of pentane vapor. Rates of mixture supply given in the text are to be taken as rates of air supply plus whatever addition of pentane vapor is required for the stated mixture strength.

Rates of oxygen reacted as given by the graphs are for pentane-air mixtures; the proportion of nitrogen is omitted from the stated composition.

Percentage concentrations of iron carbonyl stated in the text are in respect of the pentane constituent of the pentane-air mixture, the carbonyl being added as liquid to the pentane prior to vaporization.

Temperatures of reaction are taken as indicated by the "inside" thermocouple resting on the top of the reaction chamber (1, pp. 333-334).

Experimental Results

Flow configuration is the major factor determining rate of oxidation (2) and in reaction chamber No. 10 may be such that reaction is so rapid at some temperatures that measurement of rate is difficult. The configuration in the chamber is fixed by rate of mixture supply and the diameter of the admission orifice; factors which determine degree of turbulence and the velocity with which the reacting mixture impinges on the active surface. If the rate of mixture supply is too small and the diameter of the orifice too large, the velocity of the jet may not be sufficient to ensure deposition of metal rather than of metallic oxide on the surface of the chamber when the mixture contains a metallic dope such as iron carbonyl.

On the other hand, if the velocity of the jet is increased sufficiently to ensure deposition of metal on the surface of the chamber, flow configuration conditions arise which increase reaction velocities in rich mixtures to such an extent that measurement may be extremely difficult. The difficulty of choosing a suitable flow configuration is illustrated by the series of experiments described in succeeding paragraphs.

Rates of oxidation observed for the flow configuration due to passing a combining proportions pentane-air mixture through the 1.0 mm. orifice at 50 cc. per min. are given by the graphs of Fig. 1. It will be noted that iron

carbonyl in the concentration of 1.0% increases rate of reaction at all temperatures, the aldehyde hump not being eliminated on the addition of the dope, as in earlier experiments. The failure of iron carbonyl to inhibit aldehyde formation was attributed to the jet velocity being insufficient to ensure deposition of metal on the active surface of the reaction chamber, and the velocity

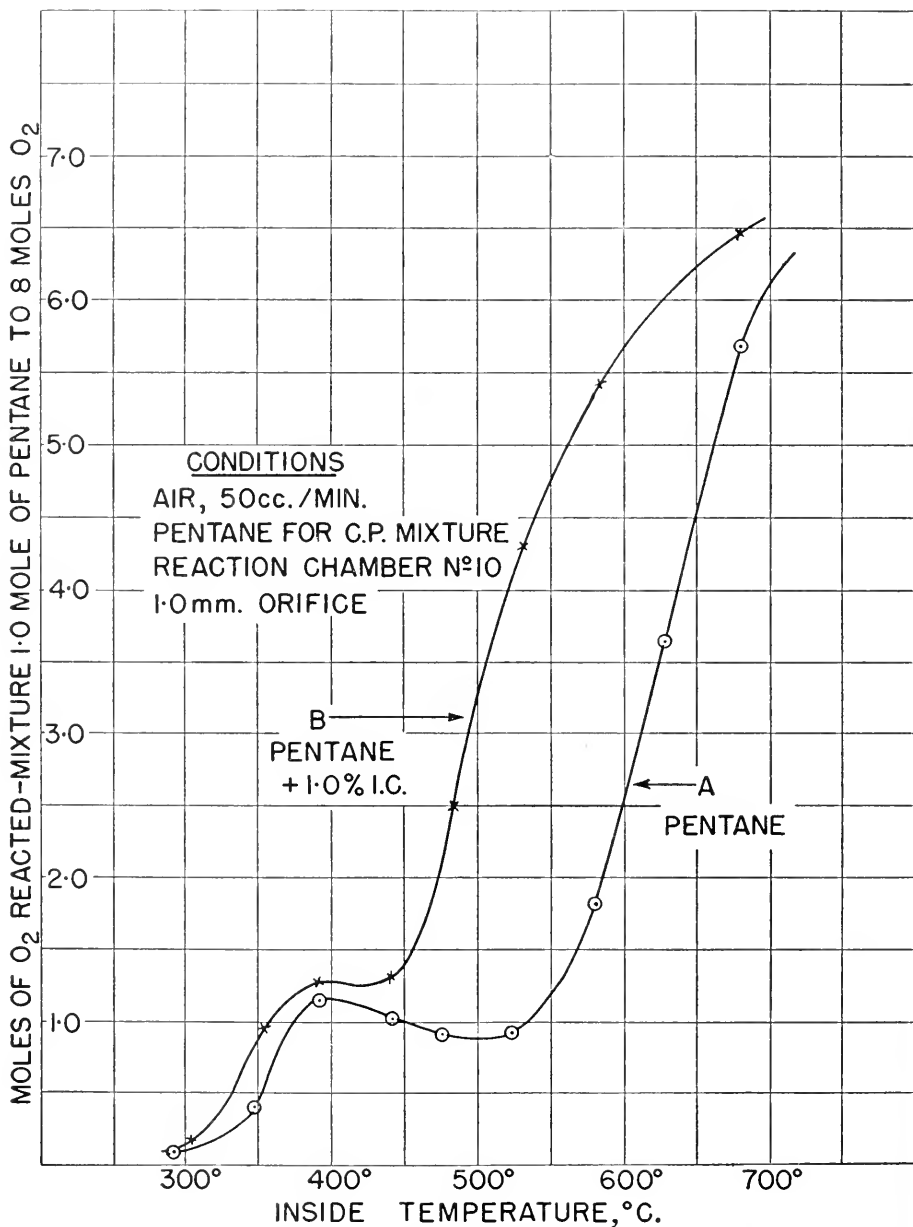


FIG. 1. Rates of oxygen reacted, pentane and pentane plus iron carbonyl for the flow configuration due to supplying a combining proportions mixture with air at 50 cc. per min.

was increased by raising the rate of mixture supply to 75 cc. per min. The experimental results then obtained are given by the graphs of Fig. 2. It will be noted, graph *B* of the figure, that the aldehyde hump has disappeared. Comparing graph *B* with the similar graph of Fig. 1, it will be seen that a

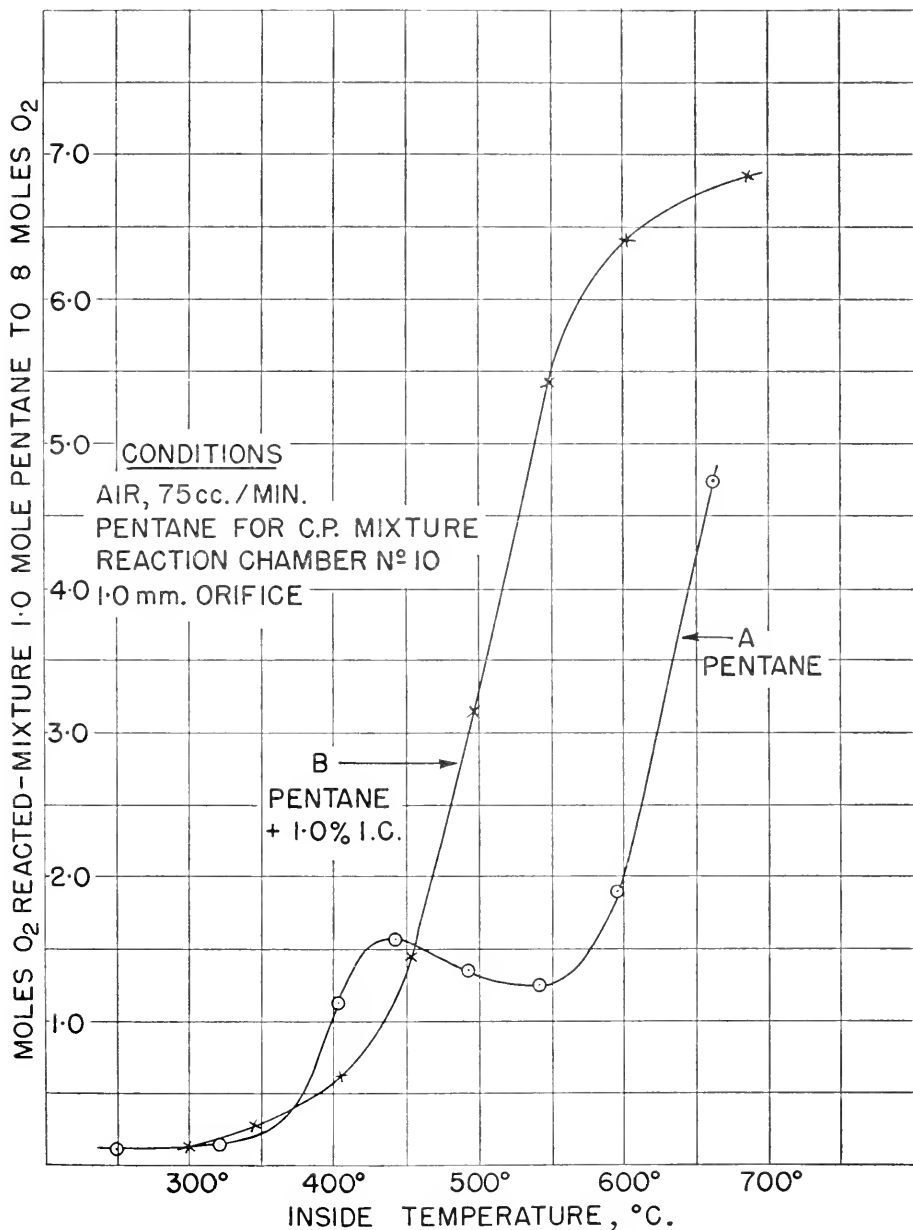


FIG. 2. Rates of oxygen reacted, pentane and pentane plus iron carbonyl for the flow configuration due to supplying a combining proportions mixture with air at 75 cc. per min.

higher rate of oxidation at temperatures above 450° C. is obtained on increasing rate of mixture supply of the *doped mixture* from 50 cc. to 75 cc. per min. On the other hand, a comparison of graphs *A* of Figs. 1 and 2 shows that, for *undoped* pentane, rate of oxidation at high temperatures diminished with increase in rate of mixture supply.

The experiments described above indicated that the flow configuration fixed by a mixture supply of 75 cc. per min. was to be preferred to that given by the lower rate of 50 cc. per min. if the characteristic effect of the dope to inhibit aldehyde formation were to be obtained. It then remained to determine rates of oxidation in the conditions if pentane were mixed with air greatly in excess of the proportion required for a "correct" mixture. The results of an experiment made accordingly are given by the graphs of Fig. 3.

Graph *A* of the figure shows that even for pentane undoped, reaction velocity was so great in a 100% rich mixture, over the temperature range 350° to 390° C. and again over the range 600° to 650° C., that observations were not obtained. Graph *B* of the figure obtained when the pentane contained iron carbonyl in the concentration of 1.0% shows a similar high reaction velocity over the high temperature range but at temperatures approximately 150° C. lower, reaction of the oxygen being substantially complete at the relatively low temperature of 550° C.

Rates of formation of carbon oxides are of interest. The graphs of Fig. 5 show that for the doped pentane, rate of formation of carbon monoxide was inappreciable, reaction being substantially to carbon dioxide and steam at any temperature. On the other hand, the graphs of Fig. 4 for pentane undoped show a rapid increase in rate of carbon monoxide formation over the temperature range above 600° C. It was demonstrated by the experiments described that reaction occurred at inconveniently high velocity when 100% rich mixtures were used.

The object of the experiments described above was to fix conditions suitable for experiments in which mixture strength would be the sole variable over the widest practicable range. It was concluded that suitable flow configuration would be set by passing the mixture through a 1.0 mm. orifice at 75 cc. per min. and that reaction velocity might not be too great if a maximum mixture strength of 50% rich were used.

Reaction velocities for a combining proportions mixture obtained when the rate of mixture supply was 75 cc. per min. are given by the graphs of Fig. 2, and the experiments were concluded by oxidations of mixtures 25% weak and 50% rich. The doped combining proportions mixture contained iron carbonyl in the concentration of 1.0% in the pentane, and, in order that the substance might be supplied to the reaction chamber at a constant rate irrespective of mixture strength, concentrations of 1.33% and 0.67% respectively in the pentane were used in the weak and rich mixtures. The experimental results are given by the graphs of Figs. 6 to 9, Nos. 7 and 8 giving rates of formation of the carbon oxides for the weak mixture. Similar graphs for the 50% rich mixture are largely duplicates of those of Figs. 4 and 5 for the 100% rich mixture and are not given.

Discussion of Experimental Results

The preliminary experiment, Fig. 1, made to determine a favorable rate of mixture supply for subsequent measurement of the effect of mixture strength on reaction velocity, discloses that conditions can be obtained in which a metallic

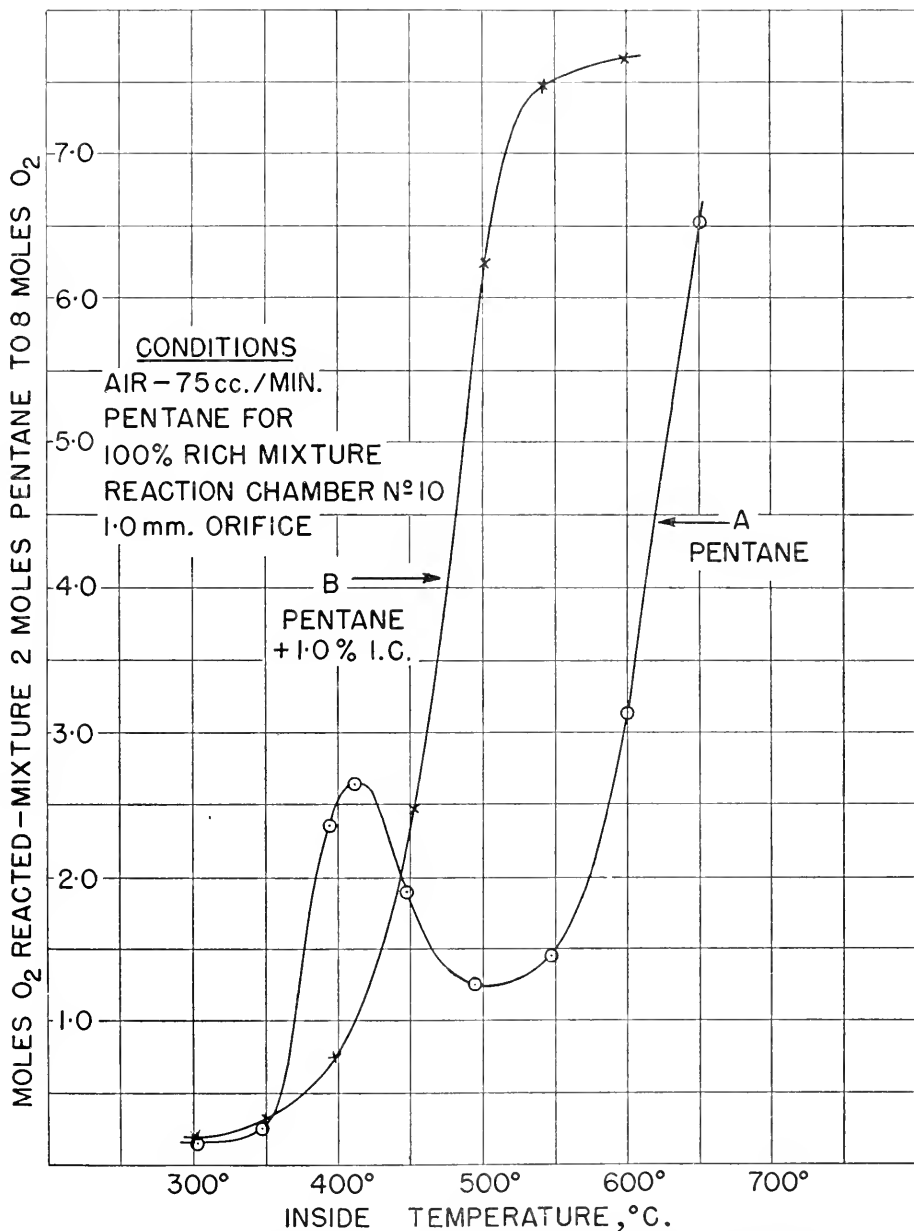


FIG. 3. Rates of oxygen reacted, 100% rich pentane-air mixture, with and without iron carbonyl, for flow configuration fixed by supplying the mixture at 75 cc. per min.

dope such as iron carbonyl promotes oxidation at all temperatures of reaction. The flow configuration consequent on supplying reacting mixture to the reaction chamber at an unusually low rate, through a relatively large orifice, was such that with the doped mixture the active surface was mainly coated with iron oxide instead of with metal as found in earlier experiments when

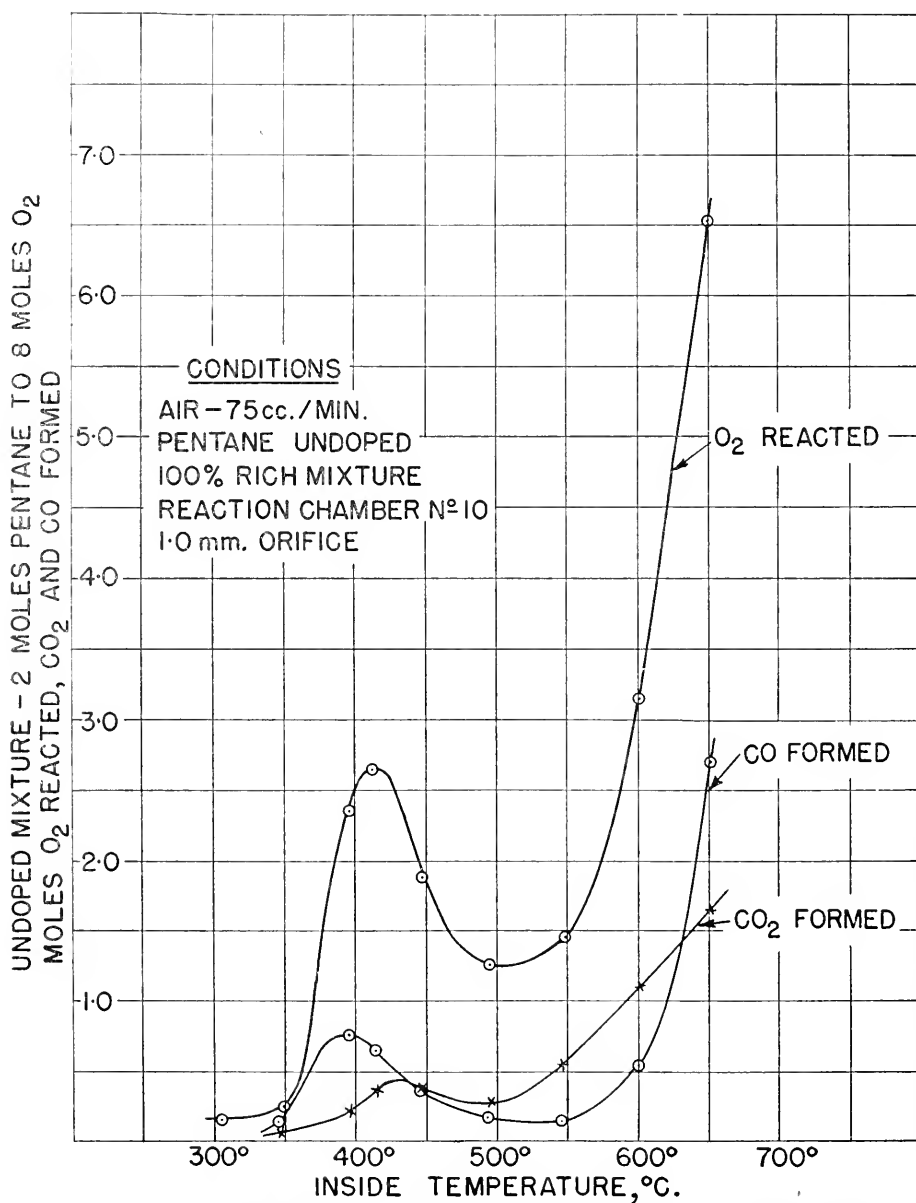


FIG. 4. Rates of formation of carbon oxides, 100% rich undoped pentane-air mixture supplied at 75 cc. per min.

using higher rates of mixture supply. The experimental results show that reaction to aldehyde as indicated by the hump on graph B, Fig. 1, proceeds at a higher rate on the oxide coated surface than on the clean glass surface, graph A, Fig. 1. The experiments show that iron oxide is most active to promote aldehyde formation when freshly formed. Thus referring to Part III

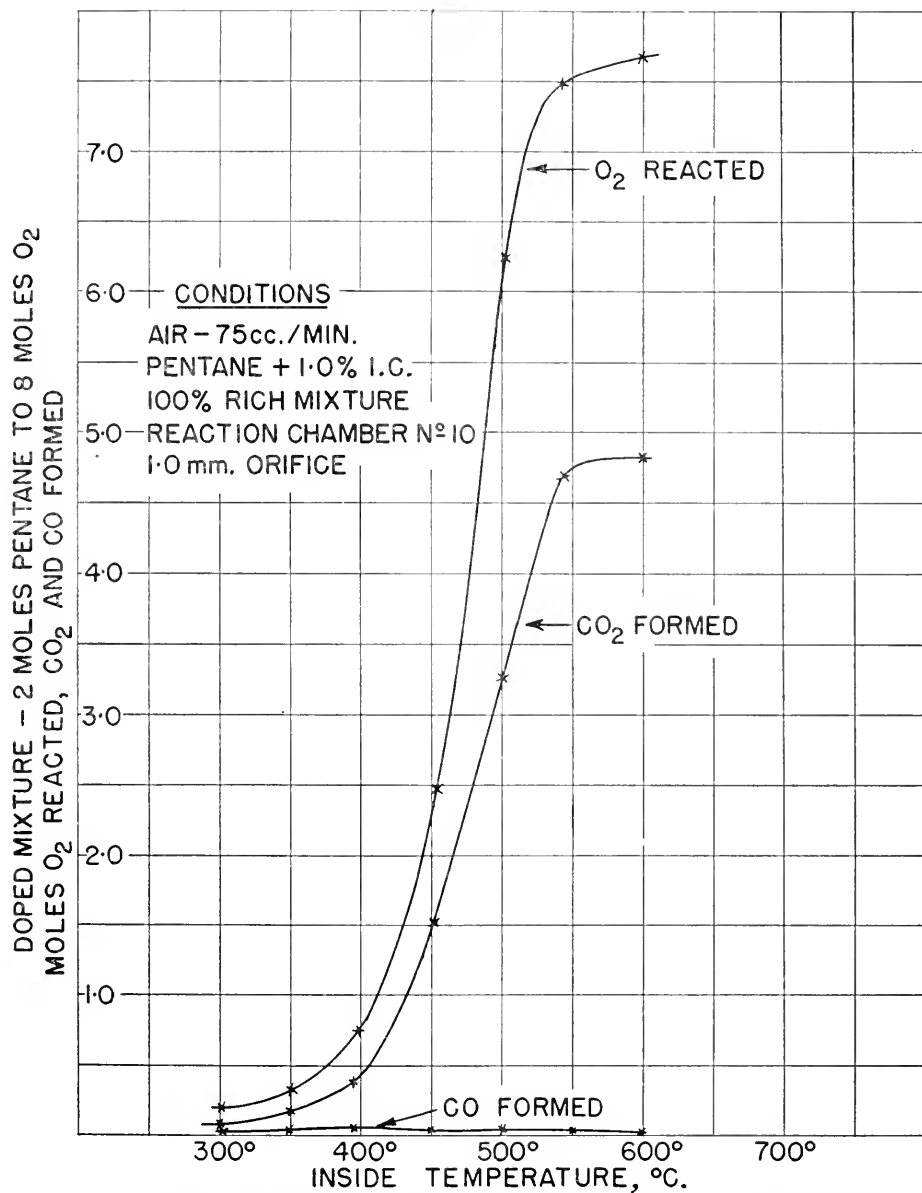


FIG. 5. Rates of formation of carbon oxides, 100% rich doped pentane-air mixture supplied at 75 cc. per min.

(3, pp. 130-131) it was shown that although aldehyde instead of final products was formed in reaction chamber No. 10 on converting the metal previously deposited on the active surface gradually to oxide, reaction velocity was less than when the surface was clean glass. On increasing the rate of mixture

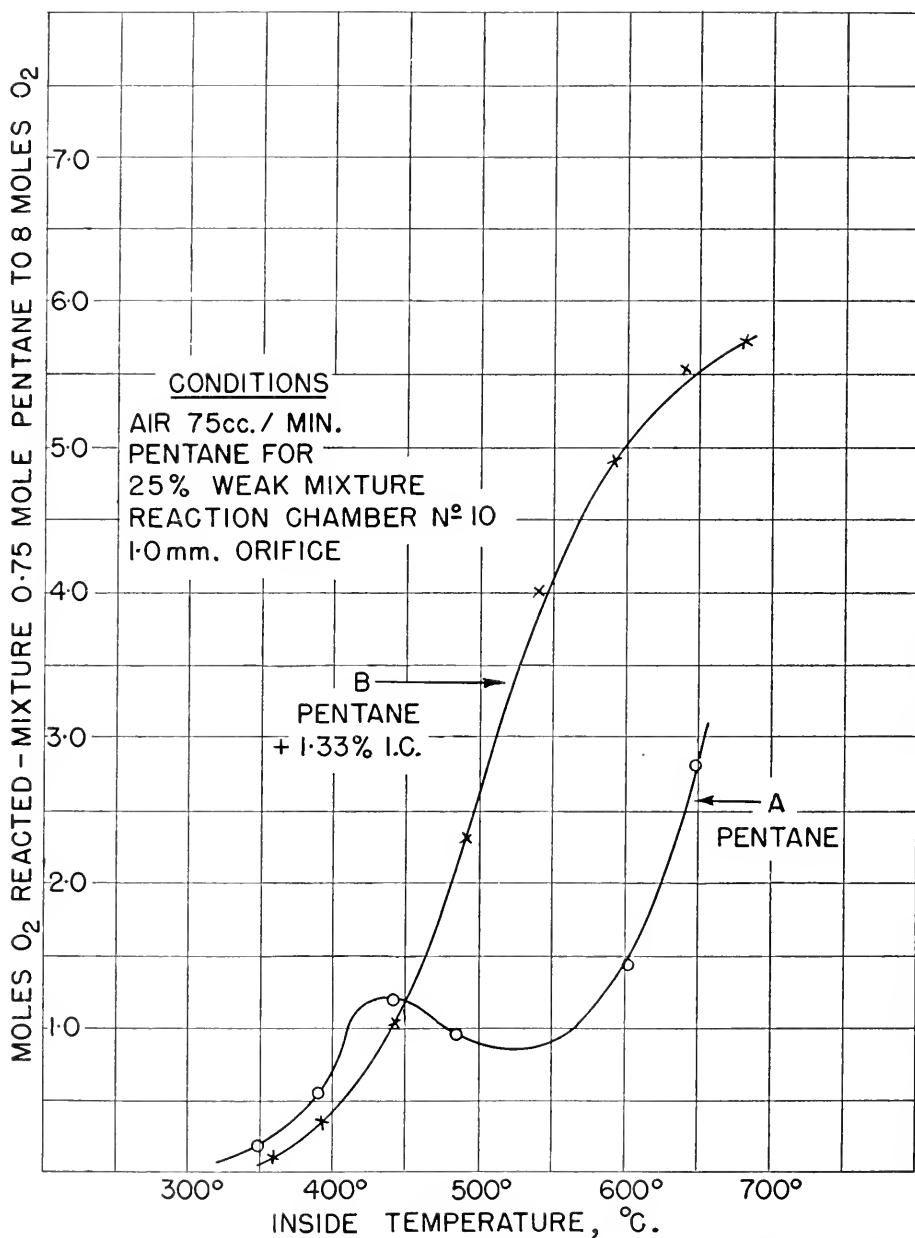


FIG. 6. Rates of oxygen reacted, 25% weak pentane-air mixture, with and without iron carbonyl, for flow configuration fixed by supplying the mixture at 75 cc. per min.

supply to 75 cc. per min. and thereby obtaining a deposit of metal on the active surface of the chamber, aldehyde is no longer obtained and reaction is to steam and carbon dioxide only, graph B, Fig. 2.

The experimental results, similarly to those given earlier (1, 2, 3), support the view that the low temperature oxidation of pentane and presumably

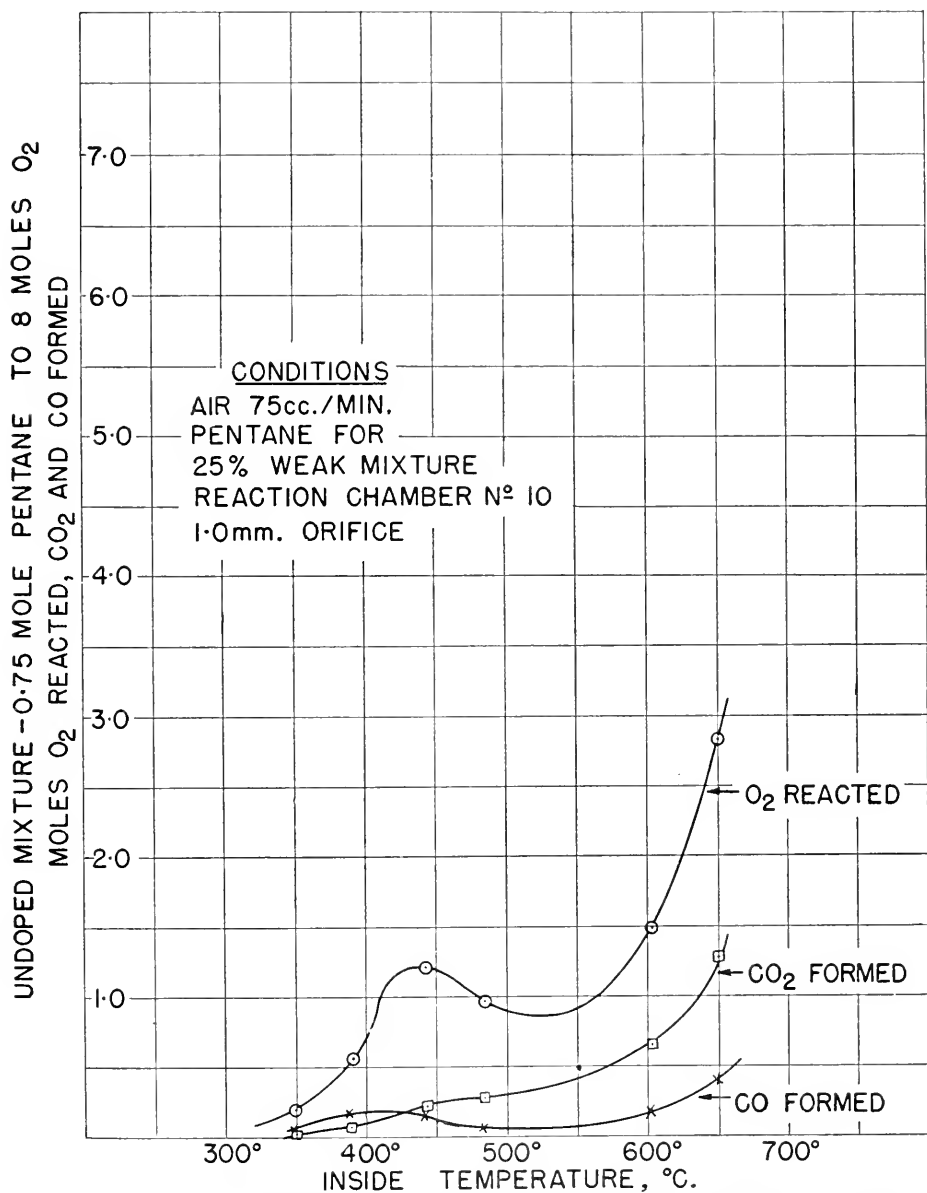


FIG. 7. Rates of formation of carbon oxides, 25% weak undoped pentane-air mixture supplied at 75 cc. per min.

similar hydrocarbons is a surface reaction; not one that can be explained by chain reaction theory. It is of interest that many attempts made accordingly have not led to any agreement in respect of the nature of the chain carriers or of the assumed unstable reaction products which are required to maintain the reaction (see review by Ubbelohde (5, pp. 2945-2947)).

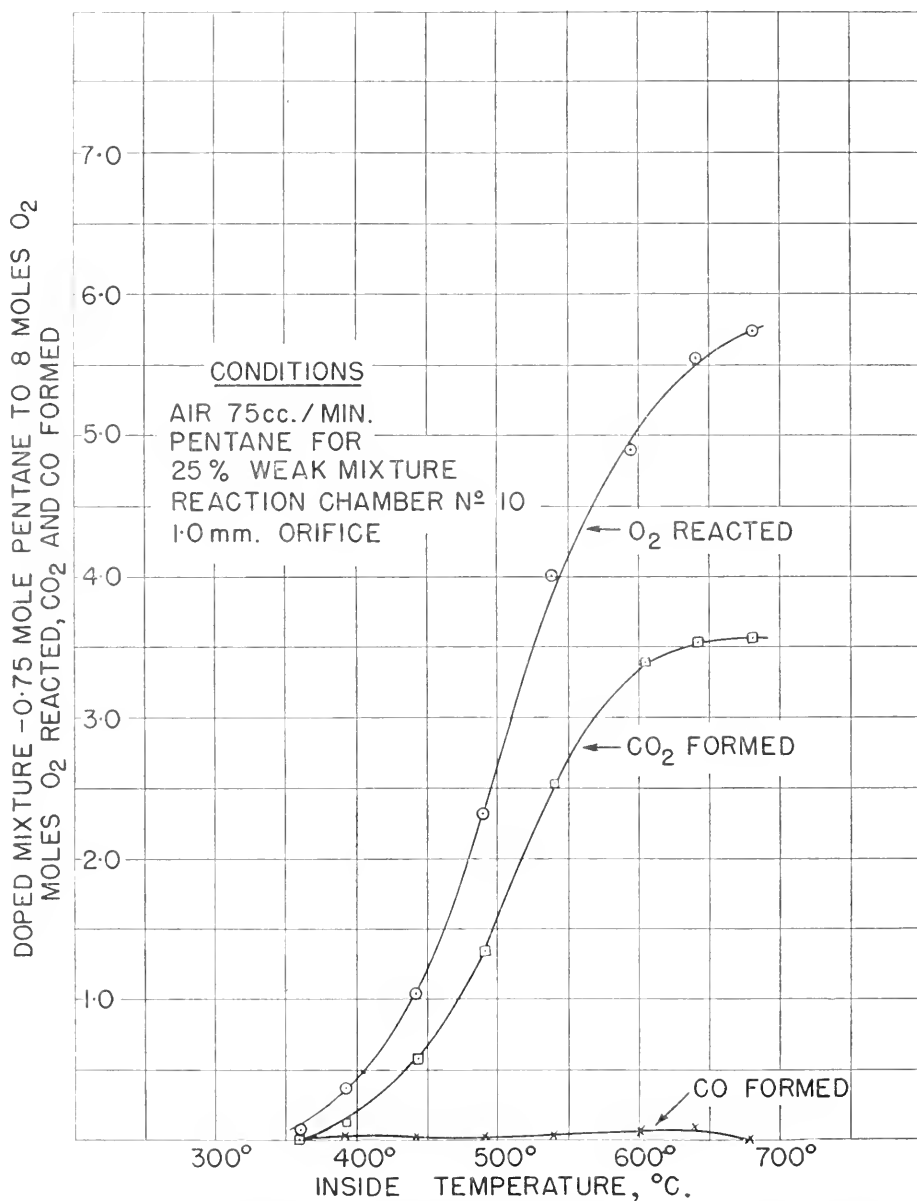


FIG. 8. Rates of formation of carbon oxides, 25% weak doped pentane-air mixture supplied at 75 cc. per min.

Mixture Strength and Reaction Velocity, Doped Pentane

Collected graphs showing rates of oxidation in weak, combining proportions and rich doped mixtures are given, Fig. 10. A remarkable increase in reaction velocity on increasing mixture strength is shown by the graphs. Thus,

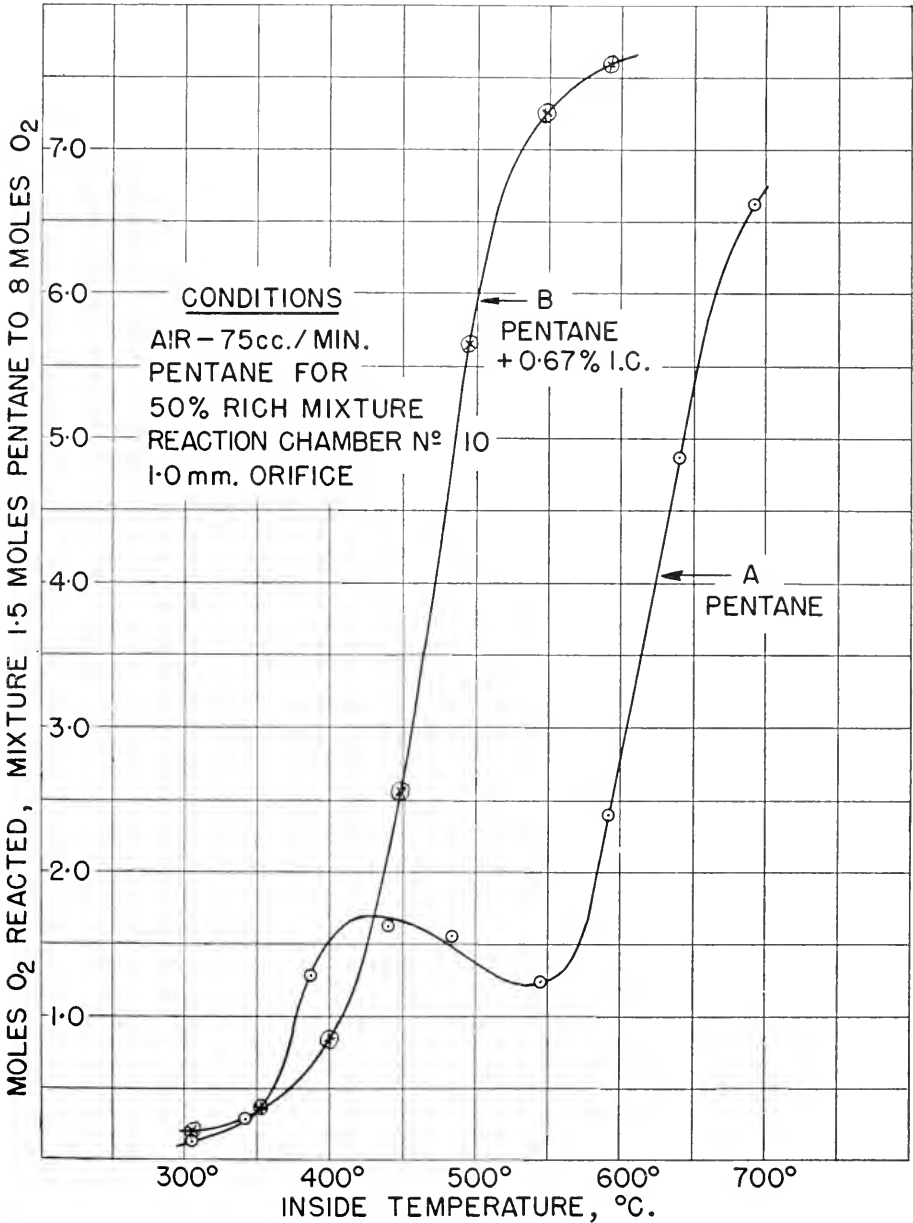


FIG. 9. Rates of oxygen reacted, 50% rich pentane-air mixture, with and without iron carbonyl for flow configuration fixed by supplying the mixture at 75 cc. per min.

substantially all the oxygen in the rich mixtures was reacted at 550° C. to form steam and carbon dioxide, graph 1, whereas in the 25% weak mixture about 5.8 moles only of oxygen out of the 8.0 moles available were reacted

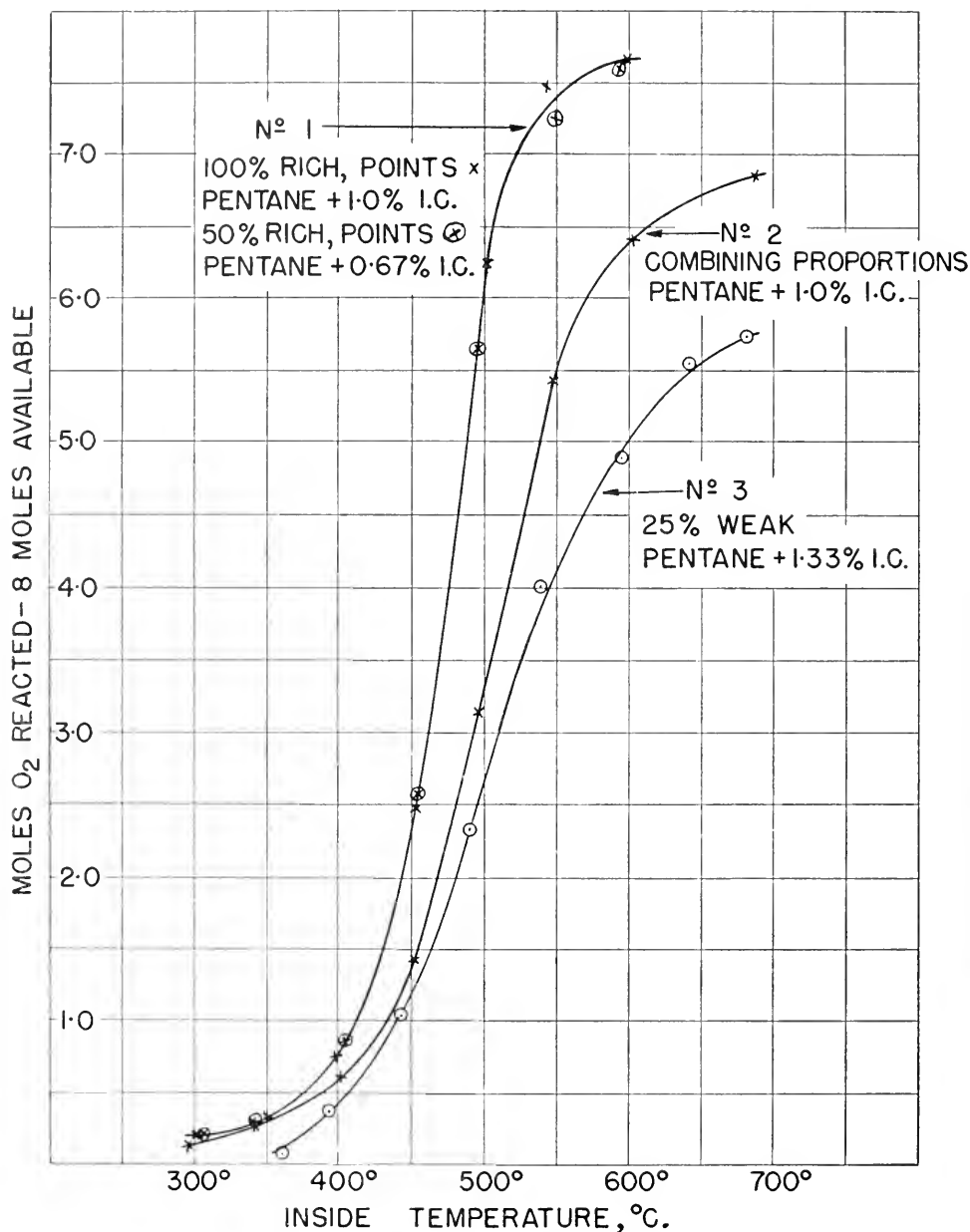


FIG. 10. Collected graphs showing that oxygen reacted for doped pentane-air mixtures reaches a limiting value, at all temperatures of reaction without explosion on increasing mixture strength and dope concentration.

even at the relatively high temperature of 690°C . Reaction velocities at low temperature are also of interest. It will be noted, Fig. 10, that reaction began at a measurable rate at about 360°C . in the weak mixture but was easily measurable at 300°C . in the richer mixtures.

Reaction velocities for a particular flow configuration reach limiting values at all temperatures of reaction on increasing mixture strength. Thus a single graph, 1, Fig. 10, can be drawn through the experimental points obtained for the 100% rich mixture containing pentane plus 1% iron carbonyl and the 50% rich mixture containing pentane plus 0.67% of the dope. Reaction in both cases was to final products only, the rate of formation of carbon monoxide being inappreciable. The consequence is that the excess pentane in both cases was not even partially oxidized and there was no visible evidence during the experiments of decomposition. It appears, therefore, that the oxidation reaction took possession of the surface, and in the circumstances there was little if any decomposition of the pentane vapor at the temperatures of the experiments. It may be, therefore, that the *decomposition* of pentane is a heterogeneous reaction at least at temperatures below 700°C .

Mixture Strength and Reaction Velocity, Undoped Pentane

The course of the reaction when pentane only is oxidized in reaction chamber No. 10 is characterized by the rate of formation of carbon monoxide for any mixture strength reaching a maximum within the temperature range 400° to 450°C . and again over the temperature range beginning at 600°C . The carbon monoxide over the low temperature range doubtless derives in large part from the oxidation of the aldehyde which is formed at a rate increasing with increase of mixture strength. Reaction velocity would not, therefore, be expected to reach a limiting value until the mixture contained pentane and oxygen in equimolecular proportions.

Reaction velocity at temperatures above 600°C . is also characterized by an increase in rate of formation of carbon monoxide as mixture strength increases, Figs. 5 and 7, but aldehyde does not appear in the products of the reaction. Velocity appears to approach a limiting value as mixture strength is increased, and the experimental results indicate that it might be attained by using mixtures more than 100% rich in pentane and obtaining equilibrium in respect of the reaction products, namely, steam and the carbon oxides.

Nature of the Oxidation Reaction

It has already been mentioned that in the experimental conditions, which are similar to those prevailing in an engine, the oxidation of pentane over the temperature range of aldehyde formation appears to be a heterogeneous reaction. The experiments also indicate that oxidation at high temperature is a reaction of the same sort. Thus the pentane vapor can be exposed to any temperature up to 700°C . while reaction proceeds with high velocity to reach a limiting value, without the occurrence of ignition or explosion. Such effects could not be obtained if the reaction were homogeneous.

Oxidation of the End Gas in an Engine as Affected by Mixture Strength

The temperature attained by the end gas varies with many conditions of engine operation but in usual circumstances temperatures are estimated to rise from about 670° to 880° C. as the compression ratio is increased from 4 to 10 : 1 if taken when combustion is 90% complete, Part IV (4, p. 233). The high temperature range of the experiments described in this part may be taken as from 600° to 650° C. although in one set of experiments nearly 700° C. was reached. Although the engine end gas temperatures are the higher, the time of exposure of the mixture in the engine is shorter than in the reaction chamber, so oxidation characteristics may be taken as similar to those found in the reaction chamber at lower temperatures. Undoped pentane being considered, relevant data taken from the *A* graphs of Figs. 2, 3, 6, and 9 are set out in Table I below.

TABLE I
MOLES OXYGEN REACTED (8 MOLES AVAILABLE) UNDOPEP PENTANE

Temperature, ° C.	Mixture proportion, pentane-air			
	25% Weak	Correct	50% Rich	100% Rich
600	1.5	2.0	2.8	3.1
650	3.0	4.2	5.4	6.5
700	—	—	6.7	—

It will be seen by reference to the table that irrespective of mixture strength an increase in rate of oxygen reacted of approximately 100% is obtained on increasing the temperature from 600° to 650° C. A further effect of especial significance in respect of detonation in the engine is that the proportion of the available oxygen reacted also increases by approximately 100% over the range of mixture strength given in the table, at either 600° or 650° C.

Acknowledgments

The experimental work described in this paper is part only of that carried out in the Colloid Science Laboratory, Cambridge University, with the co-operation of Prof. E. K. Rideal and Dr. F. H. Garner and the assistance of Mr. R. R. Davidson, Emmanuel College.

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THE OXIDATION, IGNITION, AND DETONATION OF FUEL VAPORS AND GASES

VIII. THE CAUSES OF THE ANTIKNOCK PROPERTY OF RICH MIXTURES¹

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Abstract

The engine experiments of this Part are a sequel to those of Part VII showing that enrichment of a pentane-air mixture accelerates oxidation at end gas temperatures to the antiknock substances, steam, and the carbon oxides. The corresponding antiknock effect in an engine is increased by cooling if enrichment of the mixture leads to an increase in the proportion of the fuel admitted to the engine as liquid. The engine experiments were therefore made using two fuels, *n*-pentane and a commercial fuel "S", containing high boiling point constituents. The pentane could be vaporized prior to admission to the engine and the antiknock effect due to cooling eliminated. Thus, two concurrent antiknock effects were obtained on enriching the fuel-air mixture—one due to cooling, if the fuel were admitted to the engine in part as liquid, and the other to the consequent increase in the velocity of the heterogeneous oxidation reaction in the end gas. It was also shown by the experiments of Part VII that the oxidation of rich mixtures at end gas temperatures, to steam and carbon dioxide, was greatly accelerated when iron carbonyl was added to the fuel. Similarly, the engine experiments of this Part show that the antiknock effect of enriching the fuel-air mixture is greatly enhanced when iron carbonyl is added to the fuel.

Introduction

It has long been known that the tendency of a particular fuel-air mixture to detonate in an engine reaches a maximum for a critical mixture strength and that both weaker and richer mixtures possess antiknock properties.

When using ordinary gasolines, maximum power is obtained when the mixture with air is somewhat on the rich side of the critical mixture, and a further substantial increase of mixture strength permits the use of relatively high compression ratios without detonation, though at some sacrifice of economy. Alternatively, compression ratio being fixed, as in practice, the use of rich mixtures makes possible an increase of charge density by supercharging without giving rise to the detonation which would otherwise limit the consequent power increase. Thus the fuel for supercharged aero engines is now required to give a specified increase in antiknock value, designated as "mixture response", for a particular increase in mixture strength.

The antiknock property of rich mixtures is inconsistent with currently accepted views that detonation or knocking combustion is due to an oxidation

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reaction of the chain type, beginning with the formation of organic peroxides and proceeding to explosion in a homogeneous mixture, and that metallic antiknocks act by breaking the reaction chains. Organic peroxides are formed most readily in rich mixtures (2, p. 211) and if the antiknocks acted by destroying them or in any other way breaking the chains, the efficacy of a particular concentration of antiknock would diminish with increase of mixture strength. The opposite effect is observed in practice.

The antiknock property of rich mixtures has accordingly been given scant attention in attempts to apply chain reaction theory to oxidation as it occurs in an engine and the few available references are to the cooling effect. Thus Callendar (3, p. 511) explains that overrich mixtures reduce detonation by retarding ignition and lowering the engine temperature. Egerton (5, p. 2911) after mentioning the effect of enrichment of the mixture to increase rate of oxidation, which on the basis of his chain reaction theory would *promote* detonation, attempts to dispose of the anomalous antiknock property by suggesting that the proknock effect due to oxidation is offset by an antiknock effect due to cooling. Campbell, Lovell, and Boyd (4) describe experiments showing the importance of mixture strength in respect of the rating of fuels for antiknock value but do not attempt an explanation of the observed effects. Finally, Beatty and Edgar (1) in a lengthy review of "The theory of knock in internal combustion engines", describing in detail the factors influencing the promotion or prevention of the effect, make no mention of the antiknock effect due to enrichment of the mixture or the increase in the efficacy of the metallic antiknocks when used in rich mixtures; both effects are in contradiction to the chain reaction theories advanced.

Plan and Scope of the Experiments

Ordinary liquid fuels are more or less "atomized" in the carburetor of an Otto cycle engine. Vaporization requires the addition of heat and occurs mainly in the heated induction system and in the hot cylinder, where it is assisted by the hot residual gas. Any antiknock effect due to cooling by the fuel-air mixture is caused solely by the vaporization of the fraction of the fuel entering the cylinder as liquid. Experiments were planned accordingly, using two fuels, technical grade *n*-pentane and fuel "S". The initial boiling point of the pentane was 95°F.; 90% was recovered at 96.4°F. and 95% at 97.4°F., the end point. The initial boiling point of fuel S was 85°F. and 97% was recovered at 429°F., the end point (see Fig. 1). Distillations were in accordance with A.S.T.M. procedure, D86—46.

The pentane even in rich mixtures with air could be vaporized prior to admission to the cylinder and any antiknock effect then observed on enrichment of the mixture could not be due to cooling. Fuel S could be admitted almost entirely as liquid or could be vaporized in part only with the means available, prior to admission to the cylinder. Thus by using the two fuels and varying the rate of heat addition to the mixtures with air, conditions could be

obtained in which nearly all of the fuel could be admitted to the engine as vapor or nearly all as liquid, and the consequent effects on detonation determined by varying the compression ratio to maintain a standard knock intensity.

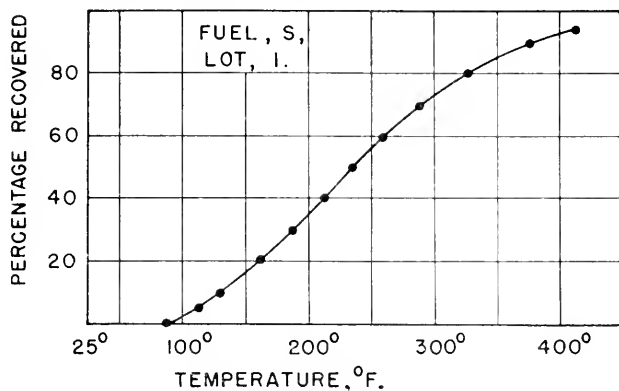


FIG. 1. Distillation range, Fuel S, Lot 1.

The scope of the experiments was extended to determine the antiknock effect of enrichment of mixtures with air of fuel S containing iron carbonyl in concentrations extending to 1.0 cc. per liter.

Experimental Arrangements

A standard C.F.R. unsupercharged variable compression engine was used for the experiments. The bore and stroke are 3.25 in. and 4.50 in. respectively and the compression ratio can be varied from 4 to 10 : 1. The engine is in universal use and further details need not be given although certain special arrangements require description.

Engine Cooling

The standard evaporative arrangement for maintaining the jacket water at a constant temperature of 212°F. was on occasion replaced by a cold tap water circulation, the flow being regulated manually to maintain any desired lower temperature.

Mixture Strength Regulation

The float chamber is flexibly connected to the carburetor, and mixture strength is varied by varying the height. When the chamber is in the "up" position, the surface of the fuel in it is level with the fuel opening into the carburetor throat, and maximum mixture strength is obtained. When the chamber is in the "down" position, the fuel level is 3.0 in. lower and mixture strength is generally too weak for engine operation. The rate of fuel consumption at a particular engine speed then depends on float chamber level, the density and velocity of the air passing through the carburetor throat, the vapor pressure of the fuel, and the diameter of a flow control orifice fitted in the fuel line from the float chamber to the carburetor.

Measurement of Mixture Strength

The C.F.R. knock testing engine is not provided with a fuel flow meter. The mixture strength required for maximum knock having a critical value for any particular fuel, the percentage variation from it can be calculated if corresponding rates of fuel consumption be measured. Fuel flow metering arrangements made accordingly were based on observations of the time required for the consumption of a particular weight of fuel, and were similar to those of the Waukesha Motor Co. (8).

Mixture Temperature and Fuel Vaporization

The air supply to the carburetor was at room temperature and humidity was not controlled. The mixture of air and liquid fuel passed from the carburetor through a heating chamber to the inlet passageway in the engine head. A requirement of the C.F.R. "motor method" of knock testing is that the combustible mixture be raised to a temperature of 300°F. prior to admission to the engine, and it is necessary in order to avoid oxidation and possible pre-ignition that the mixture be brought into contact with moderately heated surfaces of relatively large area. The effective length of the heating chamber is 7.0 in. and the inside diameter 1.72 in. Two electric heating elements each 6.75 in. long, 1.06 in. wide and 0.36 in. thick are fitted in the chamber. The area of electrically heated surface is 39.5 sq. in. and that of the surrounding surface heated by radiation is 44 sq. in. There is, in addition, about 12 sq. in. of heated induction passageway surface in the cylinder head leading to the inlet valve.

It is a requirement of the scheme of the experiments that *n*-pentane be completely vaporized prior to admission to the cylinder when the mixture temperature is 300°F. and the jacket temperature 212°F. The heat input in these conditions was 47 B.t.u. per min. and of this 6 were required to vaporize the pentane at the maximum rate of consumption and 26 to heat the air, leaving a balance of 15 for radiation and conduction. It is a fair assumption, therefore, that the mixture heating arrangements suffice to vaporize completely the *n*-pentane in a mixture with air raised to 300°F. even in the time available, when it is considered that the volume of the heater space was approximately 50% of that of the stroke volume of the engine and that the vapor pressure of the pentane at the laboratory temperature at the time of the experiments was approximately 600 mm. of mercury.

Mixture temperatures given later and on relevant graphs were as indicated by a mercury-in-glass thermometer with the bulb in a pocket in the short passageway from the heating chamber to the inlet port of the engine.

Ignition Timing

The standard C.F.R. method of changing ignition timing with change of compression ratio was used and timing was varied from 33.5° advance at 4:1 compression ratio to 14.7° advance at 10:1, but the relation is not linear as shown by the graph of Fig. 2.

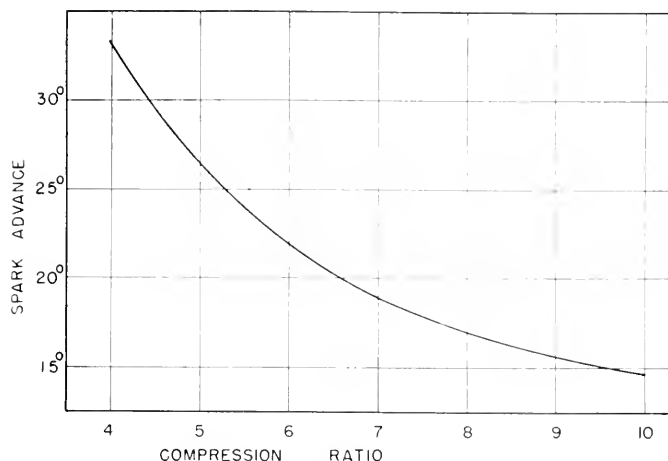


FIG. 2. Variation of spark advance with compression ratio, C.F.R. engine.

Engine Speed

The C.F.R. engine is usually arranged to drive a synchronous generator connected to an a-c. supply of constant frequency. The engine speed is thus maintained constant regardless of power output. The C.F.R. engine used for the experiments was connected by a belt drive to a d-c. generator and electrical output absorbed by a resistor bank. The engine speed was maintained at 900 r.p.m. for all of the experiments by manual regulation of the field resistance.

Standard Knock Intensity

The C.F.R. bouncing pin device and knock meter were used for determinations of an arbitrarily chosen "standard knock intensity" equivalent to that obtained in C.F.R. knock testing practice when using a standard 75 octane fuel at a compression ratio of 5.26. The calibration of the bouncing pin was always checked accordingly before starting experiments.

Inlet Valve

A shrouded inlet valve is fitted as standard to the C.F.R. engine. The valve imparts a swirl to the entering mixture but the consequent restriction reduces volumetric efficiency. It was replaced by a spare exhaust valve of the common tulip shaped variety.

Lubrication

The engine was lubricated with a commercial brand of oil, S.A.E. 30, without "additives". The oil in the crank case was maintained at temperatures between 120° and 130°F., by a manually controlled electric heater.

Experimental Results

Experiments were made with a jacket water temperature of 212°F. obtained by the evaporative cooling method already mentioned and with a jacket water temperature of 150°F. obtained by the circulation of tap water, as indicated

by a thermometer with the bulb in a pocket in the circulating water *outlet* of the cylinder head. The term "jacket temperature" is used for convenience to describe temperature conditions as above. It will be understood that the corresponding cylinder wall and combustion space surfaces are higher to an unknown extent, depending on variable heat transfer factors.

The rate of fuel consumption was varied from the minimum at which the engine would run steadily to the maximum obtainable with the C.F.R. 0.027

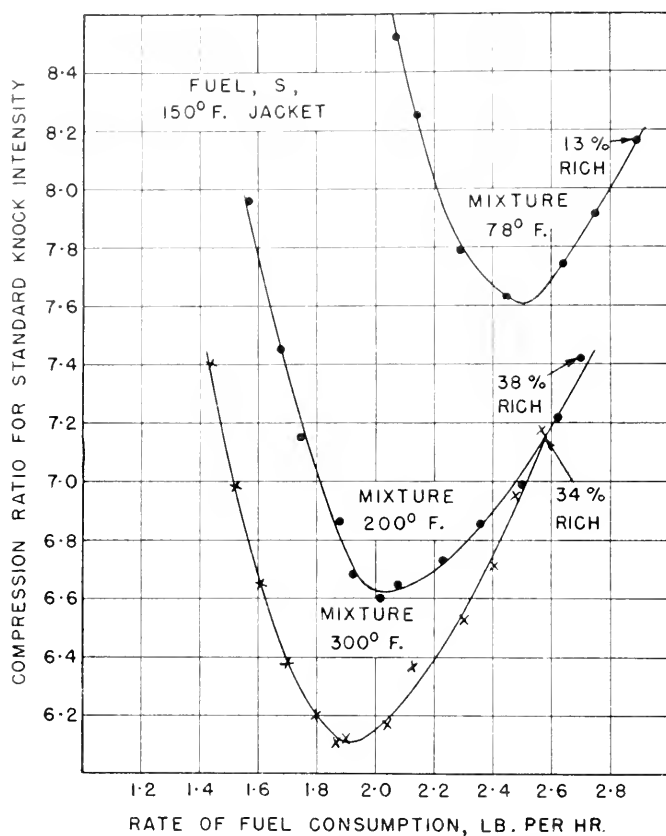


FIG. 3. Fuel S, Lot 1. 150° F. jacket temperature.

in. dia. fuel control orifice usually fitted for use with hydrocarbon fuels. Observations were thus obtained of the antiknock effects due to weakening as well as to enriching the mixture. The use of weak mixtures was of beneficial effect in burning the carbon deposited during previous running of very rich mixtures. Thus when the experiments were completed, the combustion space was found to be remarkably clean and both valves to have been seating properly. The piston rings were in good condition and free in the grooves. There was little carbon in any of the grooves. The piston crown was coated

with an adherent layer of carbon: 0.002 in. thick at the center, shading to black at the periphery and increasing in thickness to about 0.005 in.

The coating on the inlet valve was similar to that on the piston crown. There was a reddish coating about 0.005 in. thick on the exhaust valve and a similar coating on the water cooled surfaces. The color is attributed to iron oxide derived from additions of iron carbonyl to fuel S.

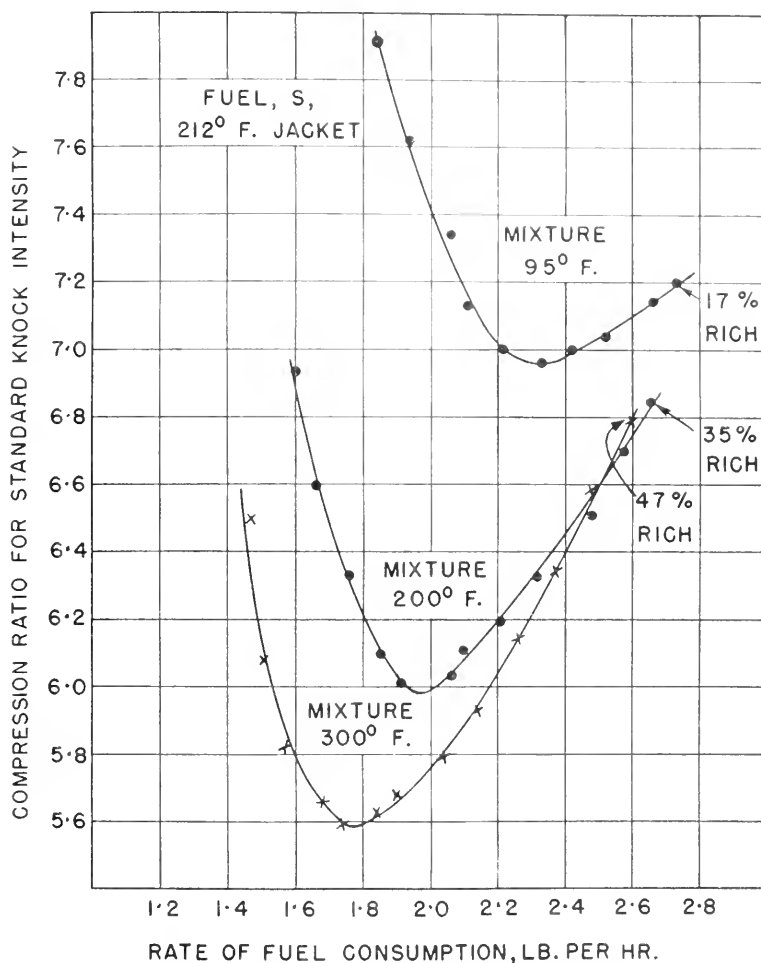


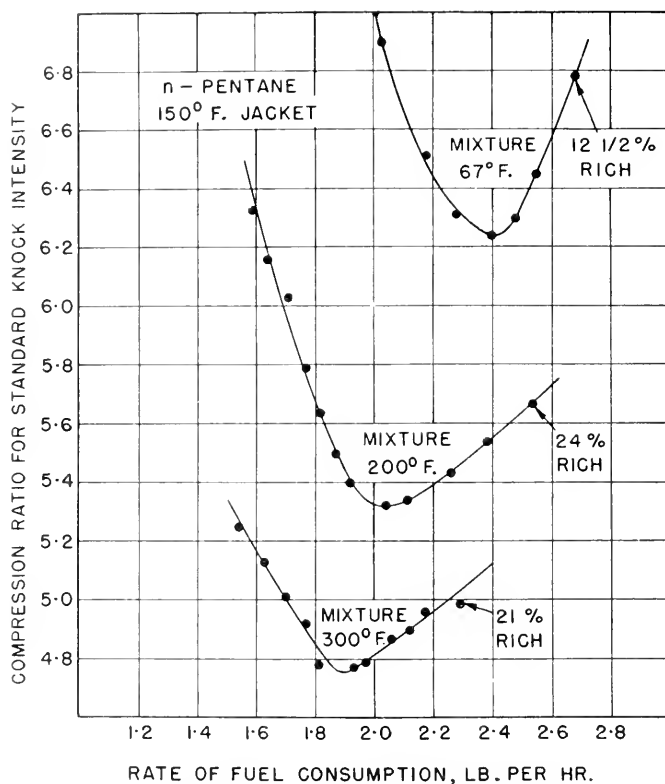
FIG. 4. Fuel S, Lot 1. 212°F. jacket temperature.

Standard intensity of knock was determined for rates of fuel consumption varying by steps over the range possible in the flow control conditions already described, with the mixture unheated, and at temperatures of 200° and 300°F. and with jacket temperatures of 150° and 212°F. The experimental results are given by the graphs of Figs. 3, 4, 5, and 6. It will be noted that the rate

of fuel consumption required for the critical mixture strength decreases with increase in mixture temperature as would be expected in view of the consequent decrease in the *weight* of air aspirated per stroke.

Experiments with Fuel S

The fuel contains volatile fractions in some proportion to provide for ease of motor car engine starting, but the graph of Fig. 1 shows that 35% only boils at temperatures below 200°F. and 74% at temperatures below 300°F. The corresponding vapor pressures and the depression in the carburetor throat determine the maximum rate of fuel consumption when the float chamber is in



[FIG. 5. *n*-Pentane. 150°F. jacket temperature.

the "up" position. The maximum rate possible with a particular diameter of flow control orifice therefore diminishes with increasing mixture temperature. Thus, referring to experiments at 150°F. jacket temperature, Fig. 3, the maximum rate of fuel consumption diminished from 2.89 to 2.56 lb. per hour as mixture temperature was increased from 78° to 300°F. In the same circumstances the rate of fuel consumption required to maintain the critical mixture strength, at which the minimum compression ratio giving standard knock intensity occurs, diminished from 2.50 to 1.90 lb. per hr. The maximum

mixture strengths obtainable varied accordingly as shown by the percentages given on the graphs.

Experiments with n-Pentane (Figs. 5 and 6)

Pentane was selected as the second fuel because of the expectation that the mixture heating means available would suffice for complete vaporization prior to admission to the engine cylinder. The experiments were made during hot summer weather and there was generally a tendency to form vapor in the fuel

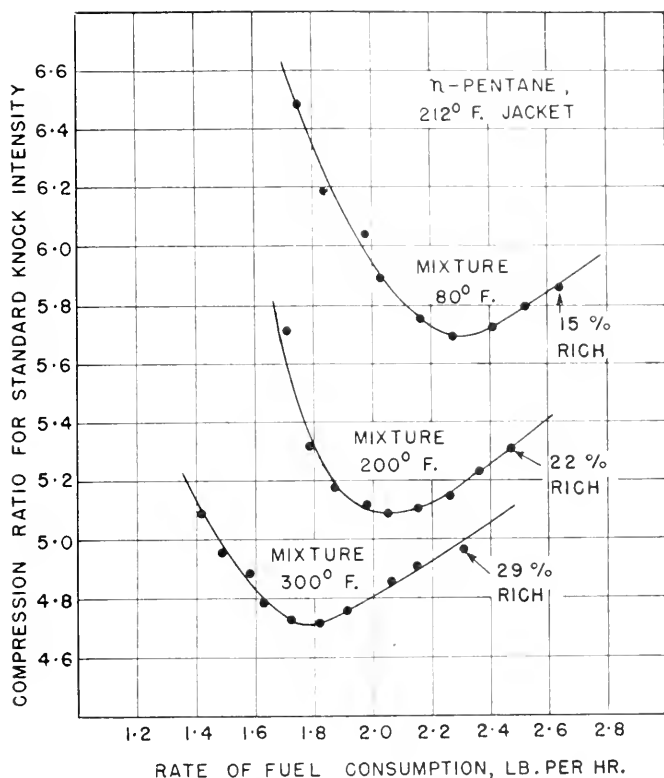


FIG. 6. *n*-Pentane. 212°F. jacket temperature.

line to the carburetor. On one occasion when the official Toronto shade temperature was 101°F., the pentane boiled in the float chamber and the experiment could not be continued.

The relatively high vapor pressure of the pentane assisted vaporization but placed a relatively low value on the maximum possible rate of consumption because of the lower than atmospheric pressure in the carburetor throat. Thus at 212°F. jacket temperature and 300°F. mixture temperature, Fig. 6, the maximum rate of pentane flow was 2.30 lb. per hr. whereas when using the less volatile fuel S the maximum flow was 2.60 lb. per hr. The degrees of

enrichment obtained in the conditions of the experiments are shown on the graph (Figs. 5 and 6 and suffice for the purpose of the investigation.

Experiments with Fuel S Doped with Iron Carbonyl

The experiments were carried out with the cylinder jacket at 212°F. and the mixture at 300°F. The fuel was from a lot of 50 gal. of old stock and differed

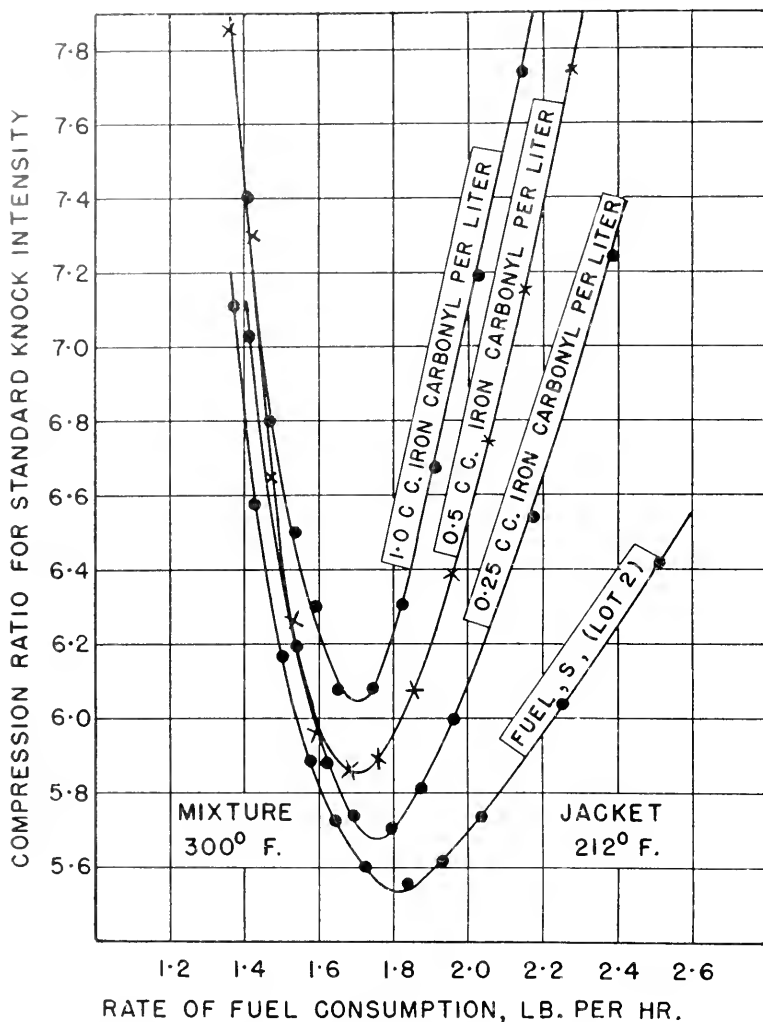


FIG. 7. Fuel S, Lot 2, and with iron carbonyl in concentrations increasing to 1.0 cc. per liter.

slightly in antiknock value and considerably in "mixture response" from that used previously which was obtained as required from a local service station.

The influence of enriching the mixture on the antiknock effect of iron carbonyl is shown by the graphs of Fig. 7. The increase in the antiknock

effect obtained on increasing mixture strength is quite remarkable. Thus the compression ratio for standard intensity of knock when using the undoped fuel at the critical mixture strength is 5.54, rate of fuel consumption being 1.8 lb. per hr. but on increasing the rate to 2.2 lb. per hr. and adding iron carbonyl in the concentration of 1.0 cc. per liter, that is, one-tenth of one per cent, the compression ratio for standard intensity of knock rose nearly 2.5 compression ratios, to 8.0:1.

Generally similar results were obtained when the fuel was doped with tetraethyl lead or nickel carbonyl. Those for iron carbonyl are presently given because the substance was used in experiments described in Part VII (7), showing that enriching the mixture increases the oxidation promoting effect of the antiknock.

Discussion of the Experimental Results

It was shown by oxidations in reaction chamber No. 10, described in Part VII (7), that over the temperature range 600° to 650°C. reaction velocity increased by 100% on enriching a pentane-air mixture from 25% weak to 100% rich. The reaction products at the high temperatures were steam and the oxides of carbon. Reaction velocity was greatly accelerated by iron carbonyl, the temperature of any particular rate of reaction being reduced by as much as 150°C., and the reaction products were steam and carbon dioxide only. The high temperature oxidation products are all antiknocks and if present in the end gas of an engine would reduce the tendency to detonation or knocking combustion as discussed in Part III (6).

The antiknock property of *rich mixtures* is indicated by the slope of the graphs for mixture strengths greater than the critical value, that is, by the ratio,

$$\frac{\text{Increase of compression ratio for standard knock intensity}}{\text{Increase in rate of fuel consumption}}.$$

The ratio will be designated by the letter, R . The experimental results summarized accordingly are given in Tables I, II, and III.

Pentane Boiling Range 95° to 97.4°F. (Table I)

The jacket temperature being 150° and the mixture temperature 67°F., $R = 2.4$; then on heating the mixture to 200°F., more of it is vaporized prior to entering the cylinder; the cooling effect diminishes accordingly and R decreases to 0.86. A further increase of mixture temperature to 300°F. reduces R to 0.70, indicating that the cooling effect has been reduced but not eliminated.

The results for a jacket temperature of 212°F. can now be considered. Starting with a mixture temperature of 80°F., the value of R is 0.70 only. It diminishes to 0.56 when the mixture is heated to 200°F. and remains un-

within the accuracy possible, on further heating the mixture to 300°F. The conclusion is that the pentane was vaporized completely when the mixture temperature was raised to 200°F, and that the value of R then obtained represents the antiknock effect arising from the increase in rate of oxidation due to increasing the mixture strength by 29%.

TABLE I
EXPERIMENTAL RESULTS—PENTANE

Jacket temp., °F.	Mixture temp., °F.	Ratio R	Jacket temp., °F.	Mixture temp., °F.	Ratio R
150	67	2.4	212	80	0.70
150	200	0.86	212	200	0.56
150	300	0.70	212	300	0.54

Fuel S, Lot 1, Boiling Range 85° to 430°F. (Table II)

The jacket temperature being 150°F. and the mixture temperature 78°F., vaporization would occur mainly in the cylinder, the maximum cooling effect would be obtained, and $R = 1.7$. The large increase of mixture temperature to 200°F. reduces R to 1.6 only and on further increasing mixture temperature to 300°F., R increases to 2.1. Thus, as the proportion of the fuel vaporized

* TABLE II
EXPERIMENTAL RESULTS—FUEL S (LOT 1)

Jacket temp., °F.	Mixture temp., °F.	Ratio R	Jacket temp., °F.	Mixture temp., °F.	Ratio R
150	78	1.7	212	95	0.6
150	200	1.6	212	200	1.6
150	300	2.1	212	300	2.5

outside the cylinder increases and the cooling effect diminishes accordingly, R increases. This characteristic is more pronounced when the jacket temperature is raised to 212°F. and the initial mixture temperature is 95°F. R is then 0.6, increases to 1.6, and to 2.5 as mixture temperatures are raised first to 200°F. and then to 300°F. That is, the antiknock effect of enrichment *increases* as the evaporative cooling effect diminishes. This characteristic is attributed to the relatively great susceptibility to oxidation of the higher boiling point constituents of the fuel.

Fuel S, Lot 2, Plus Iron Carbonyl (Table III)

The experiments were made at jacket and mixture temperatures of 212° and 300°F. respectively. The high value of R due to the susceptibility to oxidation of the heavier fractions of the fuel is then increased by the oxidation promoting effect of the metallic antiknock. The value of R increases accordingly from

1.4 for the undoped fuel to 4.4 for a dope concentration of 0.50 cc. of iron carbonyl per liter. Little further increase of R is obtained on doubling the dope concentration. This would be expected from the experimental results described in Part VII showing that the oxidation promoting effect of iron carbonyl reaches a limiting value as concentration and mixture strength are increased.

TABLE III
EXPERIMENTAL RESULTS FUEL S (Lot 2)
PLUS IRON CARBONYL, JACKET TEMPERATURE
212°F., MIXTURE TEMPERATURE 300°F.

Fuel	Ratio R
Fuel S undoped	1.4
Fuel S plus 0.25 cc. I.C. per liter	3.0
Fuel S plus 0.50 cc. I.C. per liter	4.4
Fuel S plus 1.00 cc. I.C. per liter	4.5

Conclusions

The experimental results are not in accordance with the current theory that knock or detonation in an engine is the result of an oxidation reaction in the end gas proceeding by a chain mechanism (1, 5). On the contrary, they support the view that knocking combustion tends to be prevented by dilution of the end gas with the antiknock products of the oxidation reaction occurring at the high temperature of the end gas (6), and it is concluded accordingly that:

(1) Enrichment of the fuel-air mixture used in an engine leads to an antiknock effect *in addition* to that due to the increased cooling, because of the consequent increase in the rate of oxidation of the end gas.

(2) The additional antiknock effect increases with increase in the susceptibility of the fuel to oxidation.

(3) The antiknock effect of iron carbonyl increases with increase of mixture strength because of the corresponding increase in the oxidation *promoting* effect of the substance, at end gas temperatures.

Acknowledgments

The experimental work was carried out with the co-operation of Prof. E. A. Allcut, Head of the Department of Mechanical Engineering, University of Toronto, and the cost defrayed in part by a grant-in-aid from the Defence Research Board (Canada). It is desired also to express appreciation of help

given by F. C. George F. Wright of the Department of Chemistry, University of Toronto, and by Mr. H. Shanfield of the Fuel and Oil Laboratory, National Research Council.

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THE OXIDATION, IGNITION, AND DETONATION OF FUEL VAPORS AND GASES

IX. THE CAUSE OF THE REVERSAL OF THE ANTIKNOCK PROPERTY OF RICH HYDROCARBON-AIR MIXTURES¹

R. O. KING², W. A. WALLACE³, AND E. J. DURAND⁴

Abstract

The experiments described show that conditions can be set in which a reversal of the antiknock effect of enriching a hydrocarbon-air mixture can be obtained in an unsupercharged engine. The reversal is of importance in respect of supercharged aero engines in which it may occur before mixture strength is increased to the value required for the development of maximum power. The experimental results, considered in the light of the nuclear theory of detonation, indicate that the "reversal" occurs when the rate of formation of finely divided carbon by pyrolysis of the fuel provides a proknock effect greater than can be offset by the antiknock effect of the products of the high temperature heterogeneous oxidation reaction.

Introduction

The increase in usable compression ratio obtained on increasing mixture strength is due, aside from the cooling effect, to the corresponding increase in rate of surface oxidation of the fuel to antiknock products, Part VIII (3). Dilution of the end gas by the products lowers inflammability and offsets the tendency to nuclear ignition arising from impregnation of the end gas by finely divided carbon derived from pyrolysis of the hydrocarbon fuel, Part IV (2).

The increase of end gas temperature as compression ratio is raised and an increase in the concentration of hydrocarbon fuel in the mixture with air lead to an increase in rate of pyrolysis. It would be expected, therefore, that when using fuels prone to pyrolysis in high temperature conditions of engine operation the increased tendency to nuclear ignition might cease to be offset by the decrease in inflammability of the end gas arising from dilution with the products of high temperature surface oxidation. A *reversal* of the antiknock property of rich mixtures would then occur.

The object of the experiments described in this Part was to obtain the "reversal" in the conditions in which it would be expected to occur according to the theories mentioned.

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Experimental Arrangements and Selection of Hydrocarbon Fuel

The C.F.R. knock testing engine, unsupercharged, was used for the experiments in the manner described fully in Part VIII (3). The sole change was the provision of larger diameter fuel flow control orifices as required for increasing mixture strength beyond the degree used for the standard method of knock rating.

The high temperature operating conditions expected to be required were provided by the standard A.S.T.M. - C.F.R. motor method of knock rating, that is, the fuel-air mixture was heated to 300° F. and the jacket coolant maintained at 212° F.

Preliminary experiment demonstrated that a reversal of the antiknock property of rich mixtures of normal heptane, hexane, or pentane with air could not be obtained even in the relatively high temperature operating conditions. An indication of the effect was obtained, however, when the compression ratio at which heptane could be used was increased, on the addition of tetraethyl lead.

Fuel *S* was then used for further experiments. It is a commercial gasoline of relatively high octane number as compared with *n*-pentane. The distillation graph, given by Fig. 1, Part VIII (3), shows an end point of 429° F. and that the fuel contains approximately 30% of constituents boiling above 300° F. The "heavy ends", probably long chain paraffins, would be especially prone to yield carbon on decomposition at the high temperatures of the end gas.

One set of experiments was made with fuel *S*₁, generally similar to fuel *S* but of lower initial octane number raised to exceed that of fuel *S* by being leaded. Unleaded fuel *S*₁ could not be obtained.

Experimental Results

The experimental results are given by the graphs of Fig. 1, compression ratio for standard knock intensity, described as "usable compression ratio", being plotted against rate of fuel consumption, which represents mixture strength, engine speed being constant at 900 r.p.m. The minimum value of usable compression ratio for the undoped fuel *S* was obtained when rate of fuel consumption was 1.85 lb. per hr. and it may be assumed that the mixture strength was then approximately correct. Maximum power, determined by later experiments, was obtained when rate of fuel consumption was 2.4 lb. per hr. The mixture was then nearly 30% "rich".

The reversal of the antiknock property of rich mixtures of fuel *S* undoped, Graph (1), was obtained when the usable compression ratio attained the high value of 8.2, rate of fuel consumption being then 3.7 lb. per hr. and the mixture 100% rich. On adding tetraethyl lead to fuel *S* in the concentration of 0.25 cc. per liter the "reversal" occurred at the higher usable compression ratio

of 9.3 but at the lower rate of fuel consumption of 3.4 lb. per hr., the mixture then being 84% rich. A similar "reversal" was obtained at a relatively low rate of fuel consumption when using fuel S_1 , Graph (2). Comparable results for this fuel undoped are not given because a sample was unobtainable, as already mentioned.

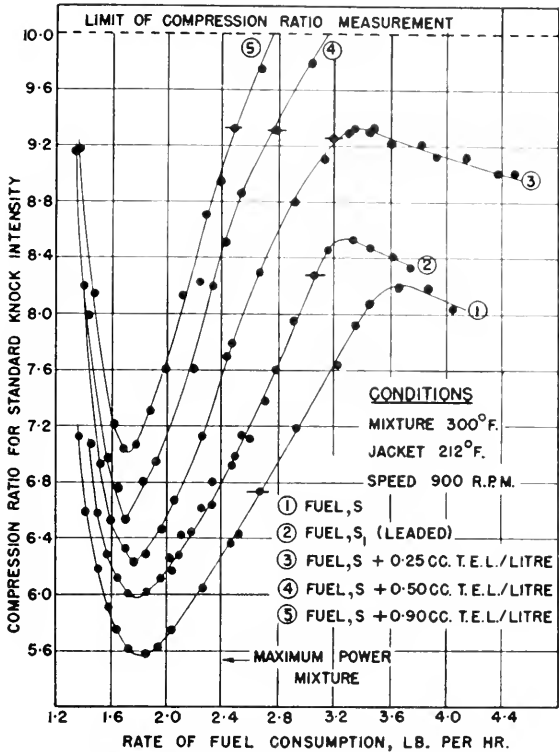


FIG. 1. Graphs showing the reversal of the antiknock effect of rich mixtures.

When tetraethyl lead was added to fuel S in the larger concentrations of 0.5 and 0.9 cc. per liter, usable compression ratio, Graphs 4 and 5, exceeded the 10:1 measurement limit before a "reversal" occurred.

The short horizontal lines on the graphs indicate the beginning of preignition which, however, never became sufficiently continuous to enable the engine to run with the spark ignition switched off.

Reversals of the antiknock property of rich mixtures were obtained when fuel S contained iron or nickel carbonyl. The experimental results were so nearly like those, shown graphically by Fig. 1, for fuel S leaded that they need not be described.

Discussion

The rate of formation of antiknock products by high temperature heterogeneous oxidation reactions in an engine is limited by the available area of active surface. On the other hand the rate of formation of proknock finely divided carbon by pyrolysis of the hydrocarbon fuel increases with the *quantity* inducted per stroke. The experiments described show that on increasing the quantity by using sufficiently rich mixtures a reversal of the antiknock effect of such mixtures was obtained in an unsupercharged engine, for the first time on record so far as known.

The reversal would be expected, according to the theory advanced, to occur in high duty supercharged engines when using leaner mixtures because the quantity of fuel inducted per stroke depends on supercharge pressure as well as on mixture strength. Thus if the combustible mixture be supplied at a pressure of say two atmospheres, the tendency to the formation of proknock carbon is doubled, other things being equal, while the rate of the heterogeneous reaction producing antiknock compounds remains unchanged. The consequence is that in supercharged aero engines, which are commonly operated in high temperature conditions, a reversal of the antiknock effect of enriching the mixture may occur even before the attainment of the mixture strength required for maximum power.

The factors leading to the reversal seem to have first received attention in Germany, and developments have accordingly been described recently by Petty, Wright, and Garner (5, 6). Recent N.A.C.A. experimental work dealing with the subject has been described by Genco and Drell (1) and by Lord, Heinicke, and Stricker (4). The cause of the reversal effect is not discussed in the references mentioned.

Acknowledgments

The experimental work was carried out with the co-operation of Prof. E. A. Allcut, Head of the Department of Mechanical Engineering, University of Toronto, and the cost defrayed in part by an extramural grant from the Defence Research Board (Canada). The liberality of Ethyl Corporation in respect of the supply of Ethyl fluid and pure tetraethyl lead is gratefully acknowledged.

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THE OXIDATION, IGNITION, AND DETONATION OF FUEL VAPORS AND GASES

X. THE CAUSE OF PREIGNITION (SURFACE IGNITION)— UNDOPED LIQUID FUEL¹

BY R. O. KING² AND E. J. DURAND³

Abstract

The theory is advanced that surface ignition, generally described as preignition, if occurring during compression, is due to partial oxidation of the fuel to aldehyde, a relatively small concentration of this inflammable substance being sufficient for ignition of the charge by the hot surfaces normally present in the combustion space of a high duty engine. The igniting effect may be early or late, that is, before or after spark ignition. Early surface ignition may cause destruction of pistons and exhaust valves of supercharged engines and is indicated by severe knocking. When the effect occurs late in the combustion period there is no destructive effect and the engine will run without spark ignition. The theory is confirmed by engine experiments with rich mixtures which oxidize readily to aldehyde, and it is shown that the occurrence of surface ignition then depends on surface and mixture temperatures. Thus in temperature conditions chosen to eliminate surface ignition, *n*-heptane can be used in the C.F.R. engine at 10:1 compression ratio and the performance of acetaldehyde does not differ from that of a hydrocarbon fuel. A conclusion of importance in practice is that early surface ignition may occur in a particular cylinder of a multicylinder supercharged engine receiving an extremely rich mixture, because of uneven distribution. If the surface ignition led to the destruction of an exhaust valve or a piston, continued running of a highly supercharged engine on the unaffected cylinders would have the disastrous consequences arising from explosion of the compressed mixture in the induction system.

Introduction

An essential condition of the type of knocking combustion frequently described as "detonation" is that the end gas be in a chemical or physical state such that flame propagation can occur in it at an abnormally high rate, otherwise combustion, already proceeding at normal velocity, would be completed without knock. It is held generally that the presensitization of the end gas is due to preflame oxidation reactions. On the other hand, according to the hypothesis advanced in Part IV (10), an abnormally high rate of flame propagation is a consequence of the end gas having become impregnated with finely divided carbon. The carbon is provided by pyrolysis of the lubricating oil when hydrogen or town gas is used as engine fuel, as demonstrated experimentally, Parts V (13) and VI (14), but mainly by pyrolysis of the fuel when liquid hydrocarbons are used.

Abnormally rapid combustion of the presensitized end gas might occur by sudden acceleration of the normal rate of flame movement as in long tubes; in the

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engine combustion space the effect can be initiated by nuclei acting as promoters of ignition or by the igniting effect of hot surfaces. Both types of ignition are shown by the high speed photographs of knocking combustion taken by Withrow and Rassweiler (21). The phenomena are shown even more distinctly by the ultra high speed photographs taken by Miller (17) and by Miller, Olsen, Logan, and Osterstrom (18).

Surface ignition, unlike the nuclear type, need not be confined to the end gas and may occur at any time after the opening of the inlet valve and is described loosely as preignition. The term would better be applied to induction ignition which seldom occurs unless initiated by the residual flame of slow burning mixtures. The term "surface ignition" is therefore applied to an igniting effect arising after the closing of the inlet valve.

When surface ignition occurs before optimum ignition timing, it is equivalent to advancing the spark and will be described as "early". When it occurs after optimum ignition timing, it is equivalent to retarding the spark and will be described as "late". The engine will continue to run on late surface ignition when spark ignition is switched off.

"Preignition" is commonly believed to be due to the igniting effect of incandescent spark plug points or patches of carbonaceous or other matter in respect of the combustible mixture as admitted to the engine cylinder. Induction ignition is possible accordingly but not the surface ignition which occurs especially when using rich mixtures after the inlet valve closes and the "hot points" have been cooled by the entering charge. Incidentally, methanol is exceptionally prone to surface ignition in spite of the cooling effect due to the high latent heat of vaporization. Thus an increase in the inflammability of the combustible mixture during compression in combination with suitable temperatures appeared to be required for promotion of surface ignition.

An increase of inflammability would be obtained on the partial oxidation of the hydrocarbon fuel to aldehyde which is known to occur during compression, and whether or not ignition then occurred would depend on the concentration of aldehyde attained and on maximum surface temperature which can be controlled, especially in a liquid cooled engine. The engine experiments to be described were planned accordingly, it being assumed as indicated by the experiments of Part II (8) that aldehyde is formed by a heterogeneous oxidation reaction and that ignition of the substance is not autocatalytic.

Experimental Arrangements

The standard C.F.R. engine was used for the experiments. Richer mixtures than usual were obtained as required by using oversize fuel flow control orifices. Knock intensity described as "standard" is defined in Part VIII (12, p. 215) and is somewhat lighter than the A.S.T.M. standard.

The fuels used for the experiments were as follows,—

Fuel S, Lot 1: Distillation range 85° to 429°F. See graph of Fig. 1, Part VIII (12), for details.

n-Pentane: technical grade, initial boiling point 91°F., dry point 100°F.

n-Hexane: commercial grade, initial boiling point 150°F., dry point 156°F.

n-Heptane: as supplied for octane number determination according to C.F.R.—A.S.T.M. procedures; boiling point closely approximates the correct value of 98.38°C. (209°F.).

Acetaldehyde: pure, boiling point, 21°C. (70.8°F.).

Preliminary Engine Experiments with the Three Paraffins and Fuel S

Temperatures of initial oxidation or combustion of pentane, hexane, and heptane taken as indicated by the appearance of peroxides, aldehyde, water,

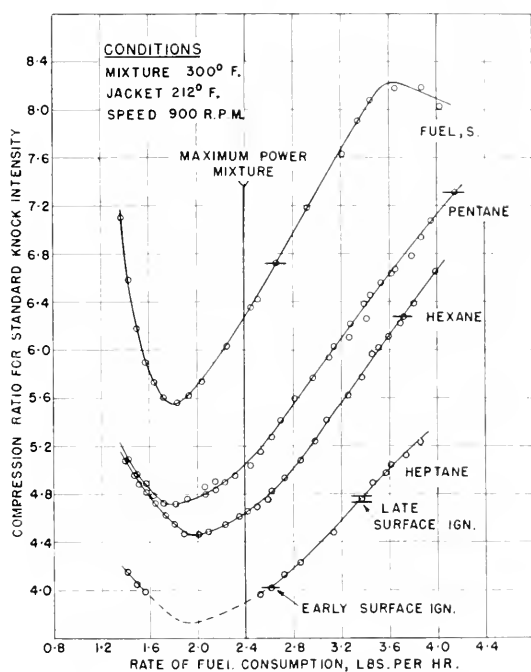


FIG. 1. Effect of mixture enrichment on the combustion of heptane, hexane, pentane and fuel S in the engine.

and carbon oxides in the reaction products, are given by Pye (20, p. 98) as 295°, 266°, and 230°C. respectively. The given values are regarded as approximate only, mixture strength not having been closely controlled.

Preliminary engine experiments using the three paraffins mentioned and fuel S were made in high temperature operating conditions, mixture strength

being continuously increased to promote surface ignition while compression ratio was increased to maintain standard knock intensity. Ignition timing was retarded as compression ratio was increased, in accordance with the C.F.R.-A.S.T.M. method of knock rating. The results of the experiments are given by the graphs of Fig. 1.

The beginning of early surface ignition is marked on the graphs by single short horizontal bars. It will be noted, as would be expected from the consideration mentioned above, that the effect occurred at decreasing mixture strength and decreasing temperature as represented by usable compression ratio, as the paraffin series was ascended from pentane to heptane.

Late surface ignition on which the engine would run without spark ignition is indicated by the pair of short horizontal lines on the graph for heptane. The effect was obtained with that fuel only. There were indications of early surface ignition when rates of heptane supply were even lower than those indicated on the graph as marking the beginning of the effect. The occasional surface ignition knock then obtained was "heavy", as would be expected. On the other hand, the late surface ignition knock observed when the engine would run without spark ignition was nearly continuous, and intensity differed so little from that adopted as "standard" that it was necessary to switch off the spark ignition to demonstrate the existence of the effect.

Cool Engine Experiments with Heptane

The preliminary experiments indicated that heptane was the most suitable fuel to use for engine experiments to be made in conditions adapted to eliminate combustion knock due to either early or late surface ignition. Further experiments were made, therefore, with the temperature of the jacket cooling water, taken at the outlet, reduced to 100°F., the heptane-air mixture unheated, and the engine speed reduced to 400 r.p.m. to reduce power and consequently the temperature gradient from the combustion space surface to the coolant. The experimental results are given by Graph *A* of Fig. 2. A second set of experiments was made in similar temperature conditions but with the engine speed raised to 900 r.p.m. The results are given by Graph *B* of the figure. Graph *C* of the figure for the heptane as used in standard C.F.R.-A.S.T.M. knock testing conditions is reproduced from Fig. 1 to show the remarkable change in performance obtained on eliminating surface ignition.

There was not the slightest indication of early or late surface ignition during the low temperature experiments, at either 400 or 900 r.p.m. At 400 r.p.m. standard knock intensity could be maintained at compression ratios rising from 1.55 to 10:1 as the rate of heptane supply was increased from 1.3 to 2.1 lb. per hr., which represents an increase in mixture strength of 62%. At 900 r.p.m. standard knock intensity could be maintained as compression ratio was raised from the minimum value of 5.3 to the measurement limit of 10, on increasing mixture strength by 50% only. It should be noted that the minimum

value of usable compression ratio is usually obtained at the "correct" mixture strength and that an increase of as much as 30% may be required to obtain maximum power.

The fuel performance obtained on the elimination of surface ignition is believed to be that governed by nuclear ignition of the end gas, and the de-

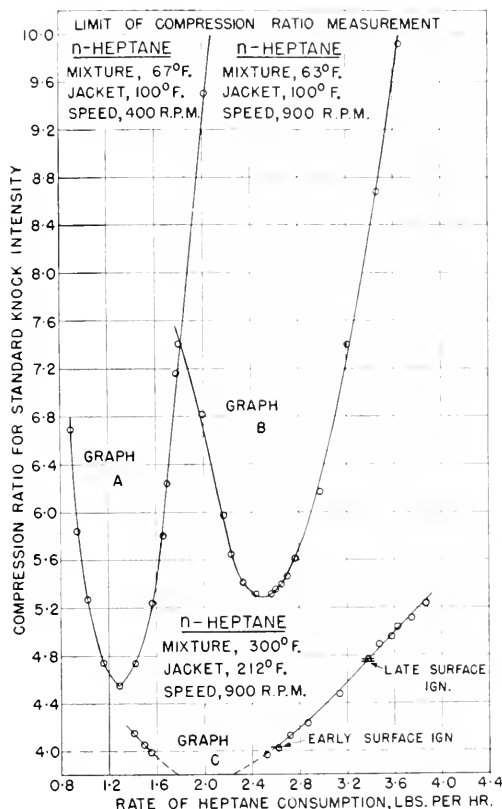


FIG. 2. Effects of surface temperature and enrichment of the mixture on the combustion of heptane in the engine.

crease of knock with increase of engine speed can then be attributed to the consequent decrease in the time available for pyrolysis of the fuel to yield the required concentration of finely divided carbon.

Engine Experiments with Acetaldehyde

Prettre (see W. Jost (7, p. 441)), discussing the luminescence of heated acetaldehyde-air mixtures, mentions that the lively combustion of the mixtures with a small surplus of aldehyde assumes an explosive form that is never observed in hydrocarbon-air mixtures and that normal ignition takes place at about 350°C. Egerton and Gates (2) obtained an igniting temperature of

395°C. on allowing a drop of acetaldehyde to fall into a heated iron pot; the igniting temperature of pentane was 515°C. in the same circumstances. It would be expected, therefore, that an acetaldehyde-air mixture would ignite prematurely if used in an engine as usually operated. Thus Egerton, Smith, and Ubbelohde (3, p. 164) state that the pure substance, b.p. 21°C., when used as fuel for an ethyl knock testing engine was "found to knock so violently that the engine could not be run".

It seemed to be possible, in the light of the experiments made with heptane, that the violent knock observed by Egerton *et al.* was due to early surface ignition and *not* to explosive combustion of the unburned mixture ahead of the flame, late in the combustion period.

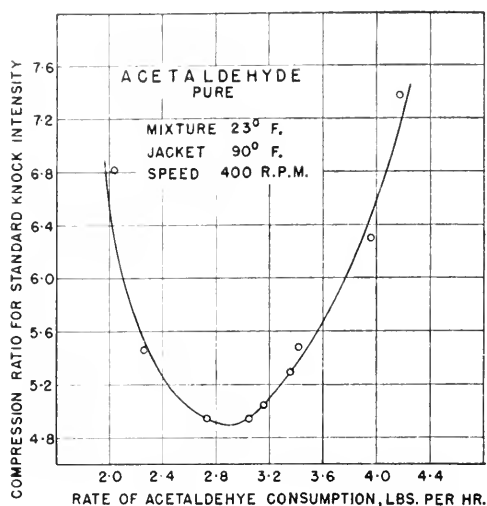


FIG. 3. The antiknock effect of mixture enrichment when pure acetaldehyde is used as fuel for the C.F.R. engine.

Experiments with the C.F.R. engine were carried out accordingly in conditions chosen to avoid surface ignition. The jacket cooling water was maintained at 90°F. and the engine run at 400 r.p.m. Furthermore, the experiments were delayed until mid-winter, when it was possible to reduce the laboratory air temperature to 55°F. The quantity of acetaldehyde available for the experiments was insufficient for a determination of the change of optimum ignition timing with change of compression ratio. A fixed ignition advance of 10° was chosen as suitable for a fast burning fuel.

The results of the engine trial are given graphically by Fig. 3. It will be seen that the acetaldehyde behaved like an ordinary hydrocarbon fuel. The minimum compression ratio, 4.9:1, with standard knock intensity was obtained when the rate of aldehyde supply was 2.9 lb. per hr. and standard knock intensity was maintained as rate of supply was increased until compression ratio

reached 7.4:1. The increase of mixture strength was then 48%, the rate of supply of 2.9 lb. per hr. being taken as corresponding to the "correct" mixture strength. The experiment was stopped at the compression ratio of 7.4:1 because frost then affected the flow from the carburetor jet; otherwise it might have been continued until the compression ratio reached the measurement limit of 10:1.

Discussion

The results of the engine experiments accord with the theory that ignition of liquid fuel during compression does not occur until the fuel has been partially oxidized to aldehyde. The results of laboratory experiments described in earlier Parts support the theory.

Thus it was shown by experiments, Part II (8), that pentane ignition temperatures as low as 515°C. and initial oxidation temperatures as low as 295°C. mentioned earlier can be obtained solely if experimental conditions are such that partial oxidation to aldehyde can occur. Turbulence was found to be the essential condition. Oxidation proceeded very slowly without that factor. Reaction was then to steam and carbon dioxide only and, in the absence of aldehyde, ignition could not be obtained even at 750°C., the limit of the indicating instrument. On the other hand, turbulence provided by convection currents in a vertical combustion tube sufficed to start oxidation at temperatures below 300°C., with profuse formation of aldehyde, Fig. 2, Part II, *loc. cit.*, and explosion occurred when the tube wall attained a temperature of 560°C.

The fuel-air mixture on passing the inlet valve of the engine, necessarily with great velocity, enters the hot cylinder and combustion space in a state of high turbulence, and the formation of aldehyde would be expected. The consequent tendency to surface ignition would not, according to the theory advanced, increase with increase of mixture strength unless rate of aldehyde formation increased accordingly. The combined effect of mixture enrichment and turbulence to increase rate of aldehyde formation was shown by experiments described in Part VII (11) using reaction chamber No. 10. The graphs relating to 25% weak, "correct", and 100% rich mixtures with air have been collected and are shown together, Fig. 4 of this Part. Air was supplied to the reaction chamber at 75 cc. per min. and pentane added as required for the stated mixture strengths. The graphs show that aldehyde is formed over the low temperature range at a rate increasing rapidly with increase of mixture strength. The maximum rate of low temperature oxidation, shown by the height of the "aldehyde hump" increased by more than 100% as mixture strength was increased from 25% weak to 100% rich, approximately the usable range in an engine. The fact that ignition did not occur is attributed to the rate of flow through the reaction chamber of 2.5 cc. volume being sufficiently rapid to remove the aldehyde almost immediately after formation.

There is, however, ample available experimental evidence respecting the formation of aldehyde during the compression of hydrocarbon air mixtures in

engines. Thus, Guldendar *et al.* (1, p. 28) demonstrated the formation of aldehyde and peroxide during compression and obtained "auto-ignition and detonation" without spark ignition when using a rich mixture of undecane with air in a Ricardo E 35 engine, the mixture being preheated to 80°C. (176°F.) and the jacket water to the same temperature. Measurements were made later by Egerton, Smith, and Ubbelohde, (3, p. 460) of the aldehyde and

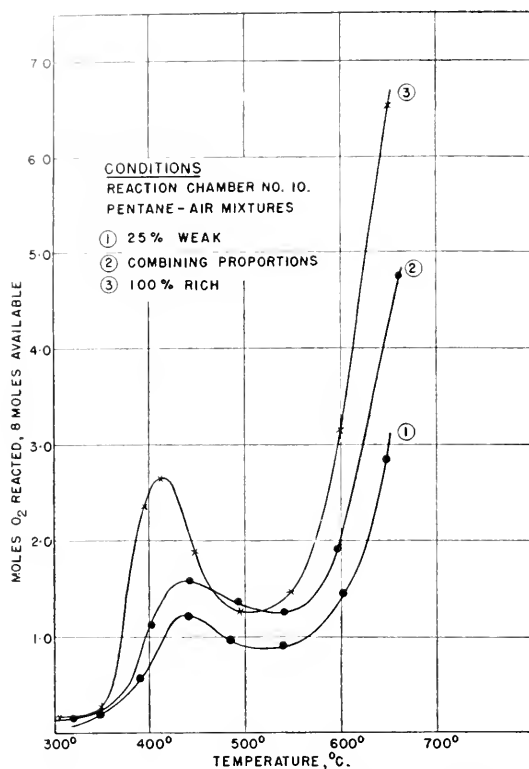


FIG. 4. Oxidation reaction rates over "low" and "high" temperature ranges as affected by increase of mixture strength.

peroxide formed during the compression stroke of an ethyl knock testing engine running at 600 r.p.m., using a jacket temperature 212°F. and unheated induction. Aldehyde was formed up to 10% by weight of the fuel although conditions in respect of mixture strength and temperature were not the most favorable. Moreover, although the engine was run under power, samples for aldehyde estimation were drawn only when spark ignition was switched off.

Concluding Comment

The conclusion arising from the experiments described in this Part, namely, that aldehyde is responsible for the preignition or surface ignition that occurs during compression, is novel, so far as known. The widely held view is that

the effect is due to the premature ignition of the fuel-air mixture, *in the state supplied to the engine*, by exceptionally hot spots in the combustion space such as spark plug points. Temperatures required are, according to Hundere and Bert (6), of the order of 2000°F. (1100°C.) for the first stages of preignition and several hundred degrees higher for very advanced preignition. They conclude that no material in the combustion space can attain the requisite temperatures without melting, other than the ceramic core of the spark plug, certain types of deposits, some from ethyl fluid, because of poor thermal contact with underlying surfaces and in some cases the exhaust valve head. Preignition occurs frequently, nevertheless, in ordinary motor car engines without surface temperatures rising to the degree required to melt an exhaust valve or an aluminum piston.

The usual method of determining preignition temperature is to heat a "temperature plug" projecting into the combustion space until ignition is obtained in advance of the spark. The extremely high "observed" plug temperature would be required unless the mixture contained excess fuel or constituents prone to oxidize to aldehyde. That is, temperatures of 2000°F. and over must have been observed in conditions in which preignition could not occur normally.

The adverse effect of uneven distribution of fuel air mixtures to multicylinder engines, in respect of power developed, has long been recognized. Accurate measurements made by Gerrish and Meem (5) show differences in mixture strength as between cylinders of a multicylinder radial aero engine of as much as 30%, and Marble, Ritter, and Miller (16) describe methods of reducing the differences with the object of increasing the possible maximum power.

The experiments described in this Part show that it is important to provide for uniform distribution in order to avoid surface ignition, which, if occurring "early" in one cylinder of a supercharged engine, may have the disastrous consequences following from the burning of the exhaust valves and piston of that cylinder while the engine continues to run on the others.

Acknowledgments

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THE OXIDATION, IGNITION, AND DETONATION OF FUEL VAPORS AND GASES

XI. THE LOSS OF POWER COINCIDENT WITH THE ANTIKNOCK ACTION OF THE CARBONYLS OF IRON AND NICKEL IN RICH MIXTURES¹

BY R. O. KING² AND EDWIN J. DURAND³

Abstract

Experiments are described which show that the increase in usable compression ratio obtained on adding iron or nickel carbonyl to rich mixtures with air, of hydrocarbon fuel used in the high temperature conditions of the A.S.T.M.-C.F.R. motor method of knock testing, is not accompanied by a commensurate increase in power. The percentage by which the observed power for the doped fuel is less than that obtainable if a nonknocking fuel were used at the same compression ratio has been determined for various additions of the iron and nickel carbonyls of Fuel S, a commercial gasoline. The loss of possible power when using iron carbonyl in the concentration of 0.50 cc. per liter, increased from 2% at maximum power mixture strength to over 22% at extremely rich mixtures. The loss is attributed to appreciable oxidation of the fuel to final products, prior to the completion of compression, especially when doped fuel is used. Thus the experimental results confirm the theory, advanced in Part III, that metallic antiknocks act by promoting the high temperature surface (heterogeneous) oxidation of hydrocarbon fuel to steam and carbon dioxide; not by inhibiting a homogeneous oxidation reaction by the breaking of reaction chains, as generally supposed.

Introduction

The theories that organic peroxides cause detonation and that the antiknock organometallic compounds act by destroying the peroxides or preventing their formation were first advanced by Callendar and associates (2, 3). The theories in one form or another are still current. Egerton and Gates (5) regard antiknocks "as negative catalysts which react with and remove those substances (peroxides) which auto-catalyse combustion". Egerton in a later publication (4) assumes that preflame oxidation in the engine is a homogeneous reaction, that it proceeds to ignition in the end gas by chain reactions, and that the metallic antiknocks act by breaking the chains. Ubbelohde (15, p. 2943) refers to "the complete inhibition of all oxidation by the addition of antiknocks". Prettre (12, p. 2956) concludes that "the influence of antiknocks in engines can only be explained by their inhibitory action on thermal combustion". Beatty and Edgar (1, p. 2934 and p. 2936) consider that "there is little evidence for the occurrence of significant surface reactions in an engine" and conclude that "antiknock agents act as inhibitors for the slow oxidation in the end gas. Their

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effect is to break some of the reaction chains and so prevent the chain development from reaching that critical point at which its multiplication begins".

The theory mentioned above is no longer tenable in view of the experiments described in Parts I (6), II (7), and III (8). They show that the products of the *decomposition* of engine fuel at *high temperatures* delay the onset of detonation or knocking combustion. The products are steam, carbon dioxide, and carbon monoxide when undoped fuels are used but when the fuel contains metallic dope the products tend to be steam and carbon dioxide only, at any temperature, and the antiknock effect is enhanced accordingly.

The difference between rates of surface oxidation of doped and undoped fuel at high temperatures and the effect of mixture strength on reaction rates were shown by experiments made when using reaction chamber No. 10 and are described in Part VII (10). Rates of reaction were found to increase by 100% on raising the temperature from 600° to 650°C. and to increase by 100% at any temperature within the range, on increasing mixture strength from 25% weak to 100% rich. Nearly 20% of the oxygen in the weak pentane-air mixture passing through the chamber was reacted at 600°C., and 80% of the oxygen in a 100% rich mixture was reacted at 650°C. Similar rates of reaction but at *temperatures 150°C. lower* were obtained when iron carbonyl was added to the pentane.

Temperatures attained by the end gas in an engine when combustion is 90% complete are estimated to be somewhat greater than 650°C. even at the low compression ratio of 4.0 (9, p. 233), and during the whole of the combustion period the "skin" surface temperatures which determine the velocity of surface oxidation would be higher to an unknown degree, because of radiation from the flame. Surface oxidation prior to completion of compression would result in a loss of power. The greater loss would occur if oxidation were promoted to final products by the use of metallic antiknocks, especially as reaction would then proceed at high velocity even at temperatures as low as 430°C. (9, p. 438).

Thus the experiments described in this Part show the *difference* in the effects on power and knock, due to surface oxidation, as between Fuel S and the same fuel containing iron or nickel antiknocks.

Section 1

EXPERIMENTAL ARRANGEMENTS AND RESULTS

The C.F.R. knock testing engine used for the experiments was "standard" except that arrangements were made for accurate measurement of power output.

The belt driven main and auxiliary generators of the C.F.R. unit were disconnected from the engine. The main generator was then driven as a motor from the laboratory d-c. supply and it in turn drove the auxiliary generator which supplies current for the engine auxiliaries, such as the bouncing pin, the

oil heater, the intake air heater when used, and the ignition system. The engine was then direct connected to a d-c. swinging field dynamometer with beam type scale. Thus, net brake horsepower was measured. Indicated horsepower was obtained by adding, to the B.H.P. observed when the engine was developing power, the brake horsepower required to overcome friction and pumping losses when fuel was not added to the air supply and the engine was "motored" by the dynamometer. "Motoring" loss was measured after every set of power observations as soon as possible after stopping the fuel supply.

All the experiments to be discussed were made in the conditions of the C.F.R.-A.S.T.M. motor method of knock testing; mixture temperature, 300°F.; jacket coolant temperature, 212°F.; and engine speed, 900 r.p.m.

Fuel *S*, Lot 2, a commercial grade of gasoline, generally similar to Fuel *S*, Lot 1 (11, pp. 212-213), was used for the experiments.

The experimental results are given by the graphs of Figs. 1 to 5. A uniform system of lettering is used. Thus variation of the compression ratio for standard knock intensity with increase of mixture strength is shown for the doped fuel by the *A* graphs and for the undoped fuel by the *A*₁ graphs. The variation of indicated horsepower (I.H.P.) with increase of mixture strength is shown for the doped fuel by the *B* graphs and for the undoped fuel by the *B*₁ graphs.

The term "usable C.R." will be used hereafter as an abbreviation of "compression ratio for standard knock intensity", as defined in Part VIII (9, p. 215).

It is shown by the *A*₁ graphs that the minimum value of the usable C.R. was obtained when the rate of fuel consumption of the undoped fuel was 1.85 lb. per hr., and, as explained in Part IX, it may be assumed that the fuel-air mixture was then approximately "correct" and consequently that percentages by which the mixture strength is rich or weak can be calculated accordingly for other rates of fuel consumption.

NICKEL CARBONYL ADDITIONS TO FUEL *S*

Concentration: 0.25 cc. per Liter of Nickel Carbonyl. Fig. 1

The graphs of Fig. 1 show that nickel carbonyl in the concentration in the fuel of 0.25 cc. per liter is of slight effect to increase the usable C.R. at correct mixture strength and that there is no increase of power.

Maximum power is obtained at a rate of fuel supply of 2.3 lb. per hr., that is, with a mixture strength 24% rich. The value 4.02 I.H.P. is the same for both fuels within the accuracy of measurement, although the usable C.R. for the doped fuel was 6.5 and for the undoped fuel 6.07. That is, an increase of 0.43 in usable C.R. obtained on adding the nickel carbonyl was not accompanied by any increase of power.

It will be noted that for rates of fuel consumption exceeding 2.5 lb. per hr. the large increases in usable C.R. obtained accordingly were accompanied by relatively large decreases in power.

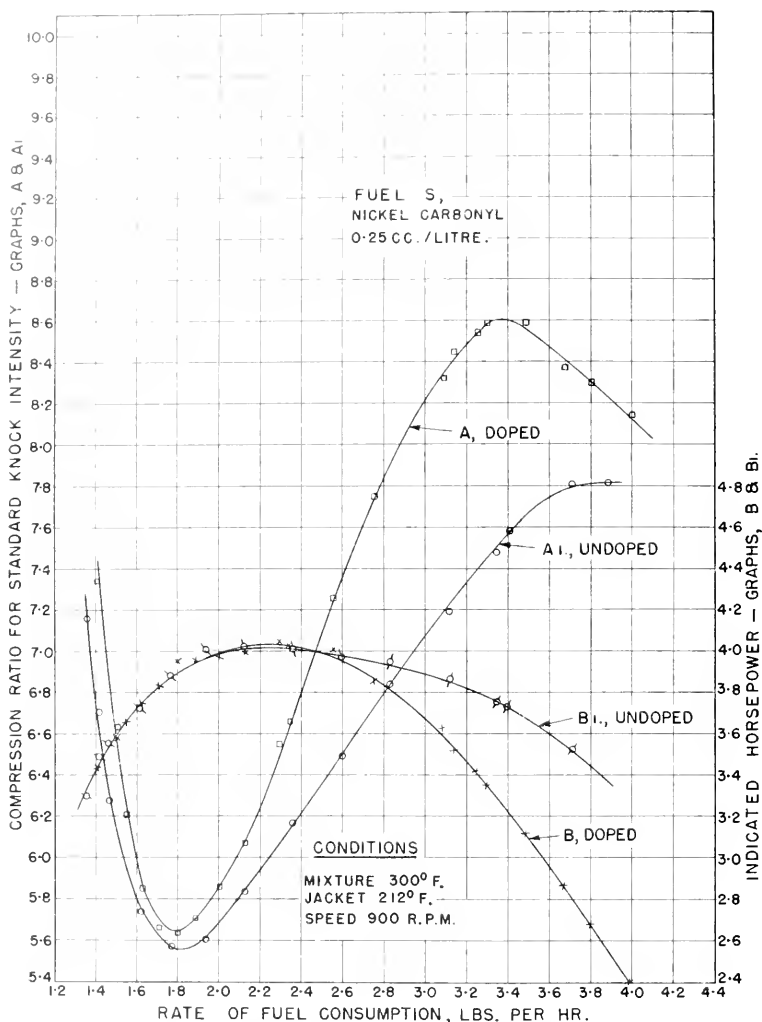


FIG. 1. The relation between usable compression ratio and power as affected by nickel carbonyl in the fuel in the concentration of 0.25 cc. per liter.

Concentration: 0.50 cc. per Liter of Nickel Carbonyl. Fig. 2

The effects on power and usable C.R. are shown in the graphs of Fig. 2. At the maximum power mixture strength, 2.3 lb. of fuel per hr., an increase of from 4.02 to 4.18 I.H.P. is obtained for a usable C.R. increase of from 6.07 to 6.80. The beneficial effect on power diminishes with further increase in mixture strength although usable C.R. increases rapidly, and when rate of fuel

consumption reaches 2.9. lb. per hr. the power developed by the doped mixture at a usable C.R. of 8.34 is the same as that for the undoped fuel at a usable C.R. of 6.92. The mixture strength being still further increased, usable C.R. increases accordingly but the power becomes *less* than for the undoped fuel at very much lower usable compression ratios.

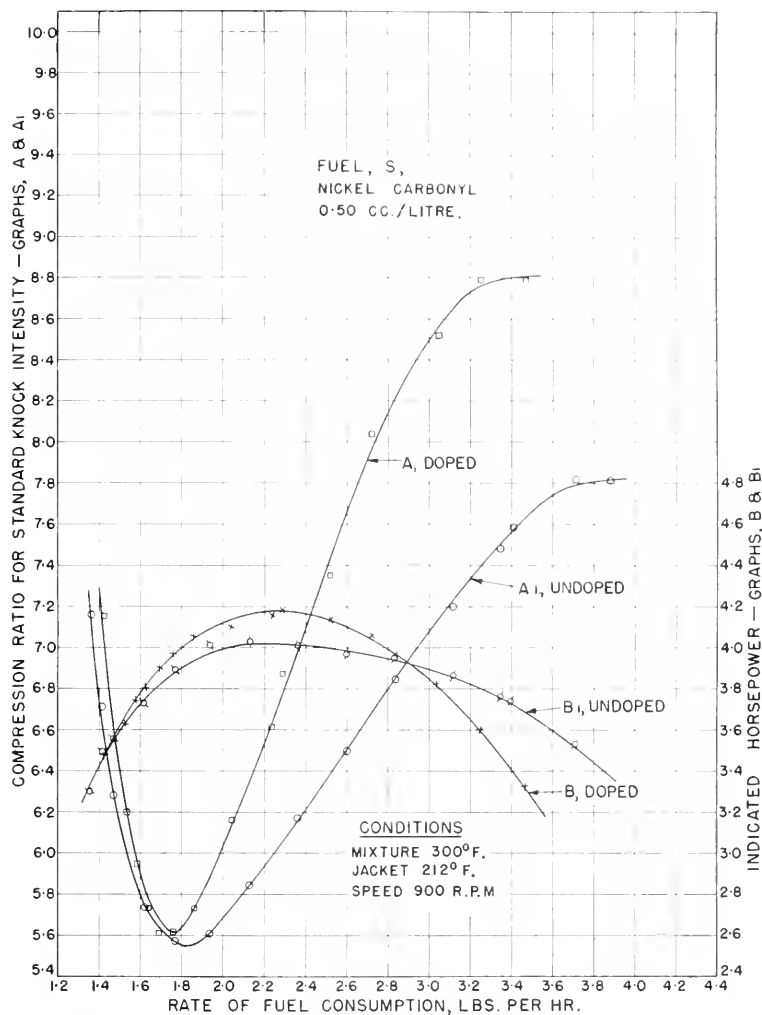


FIG. 2. The relation between usable compression ratio and power as affected by nickel carbonyl in the fuel in the concentration of 0.50 cc. per liter.

Concentration: 1.0 cc. per Liter of Nickel Carbonyl. Fig. 3

The effects on power and usable C.R. are shown by the Graphs of Fig. 3. At the maximum power mixture strength, 2.3 lb. of fuel per hour, I.H.P. increases from 4.02 to 4.34 for the very large increase in usable C.R. of from 6.07 to 7.85.

A usable C.R. of 10, the limiting value for the engine as used, was attained for the doped fuel at 6.92, the rate of fuel consumption to 2.9 lb. per hr. The increase in usable C.R. from the 6.92 of the undoped fuel was accompanied by an increase of from 5.02 to 4.15 I.H.P., that is, less than 6%.

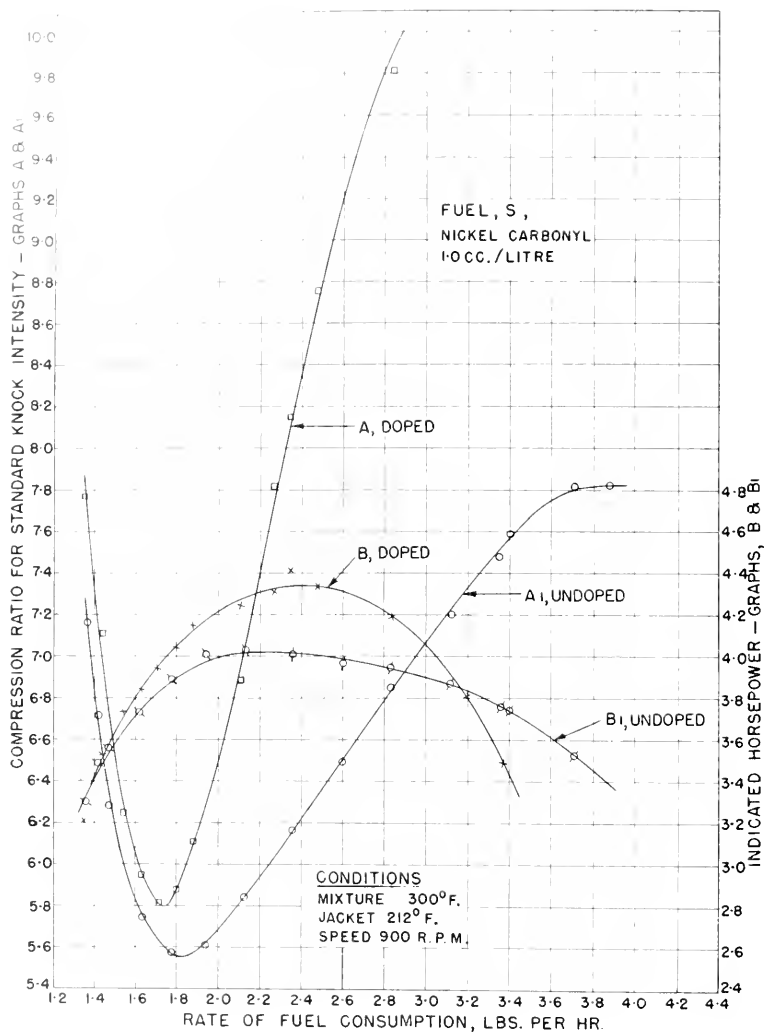


FIG. 3. The relation between usable compression ratio and power as affected by nickel carbonyl in the fuel in the concentration of 1.0 cc. per liter.

Equal power was developed by the doped and undoped fuels at a fuel consumption of 3.17 lb. per hr. The usable C.R. for the undoped fuel was then 7.25 but that for the doped fuel was greater than 10.

IRON CARBONYL ADDITIONS TO FUEL S

Concentration: 0.25 cc. per Liter of Iron Carbonyl. Fig. 4

The effects on power and usable C.R. are shown by the graphs of Fig. 4. The antiknock effect of the iron in respect of weak mixtures is noteworthy. Thus the minimum value of the usable C.R. 5.68 was observed when the rate

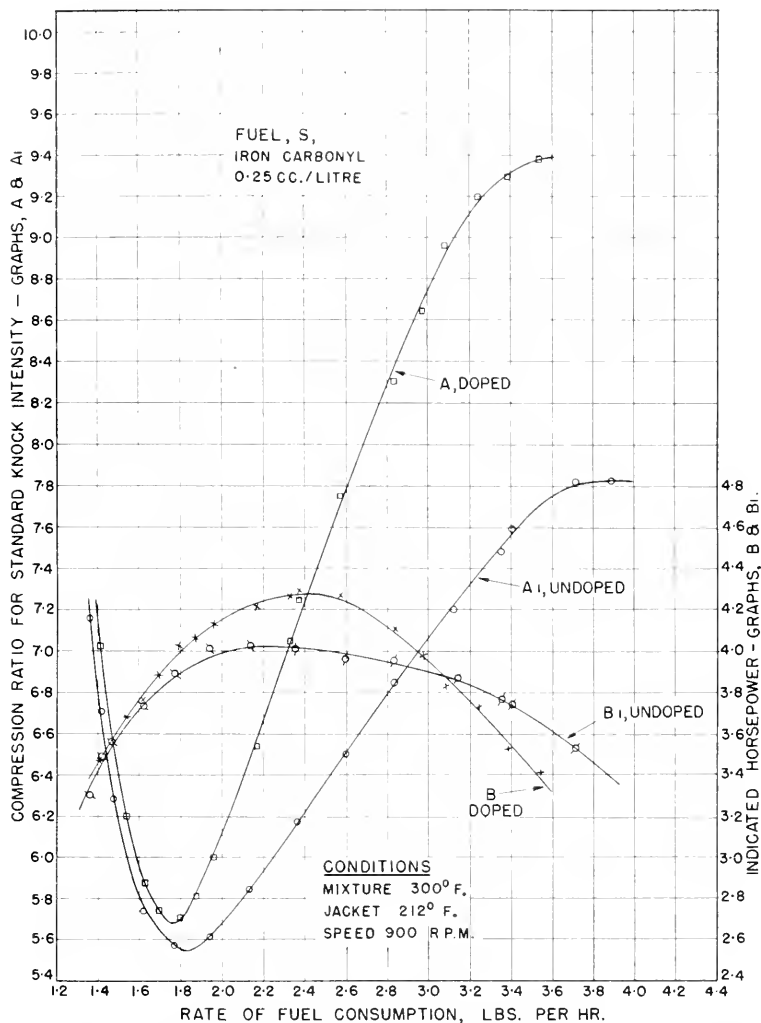


FIG. 4. The relation between usable compression ratio and power as affected by iron carbonyl in the fuel in the concentration of 0.25 cc. per liter.

of doped fuel consumption was 1.76 lb. per hr., whereas when Fuel S was used undoped, the minimum usable C.R. was 5.54, observed for a rate of fuel consumption of 1.85 lb. per hr. The I.H.P. for the undoped fuel used at 1.85 lb. per hr. was 3.93 and for the doped fuel 4.04 at the same rate of fuel consump-

A power increase of 2.8% was obtained on increasing the usable compression ratio from 6.21 to 7.28.

A maximum I.H.P. of 4.28 was obtained for the doped fuel when the rate of fuel consumption was 2.1 lb. per hr.; the usable C.R. being then 7.28. The I.H.P. for the undoped fuel at the same rate of consumption was 4.0; the usable C.R. being then 6.21; that is, a power increase of 7% was obtained on increasing the compression ratio from 6.21 to 7.28.

The same I.H.P., namely 3.9, was obtained for both fuels when the rate of consumption was 3.1 lb. per hr. although the usable C.R. for the doped fuel was 8.95 as compared with 7.2 for the undoped fuel.

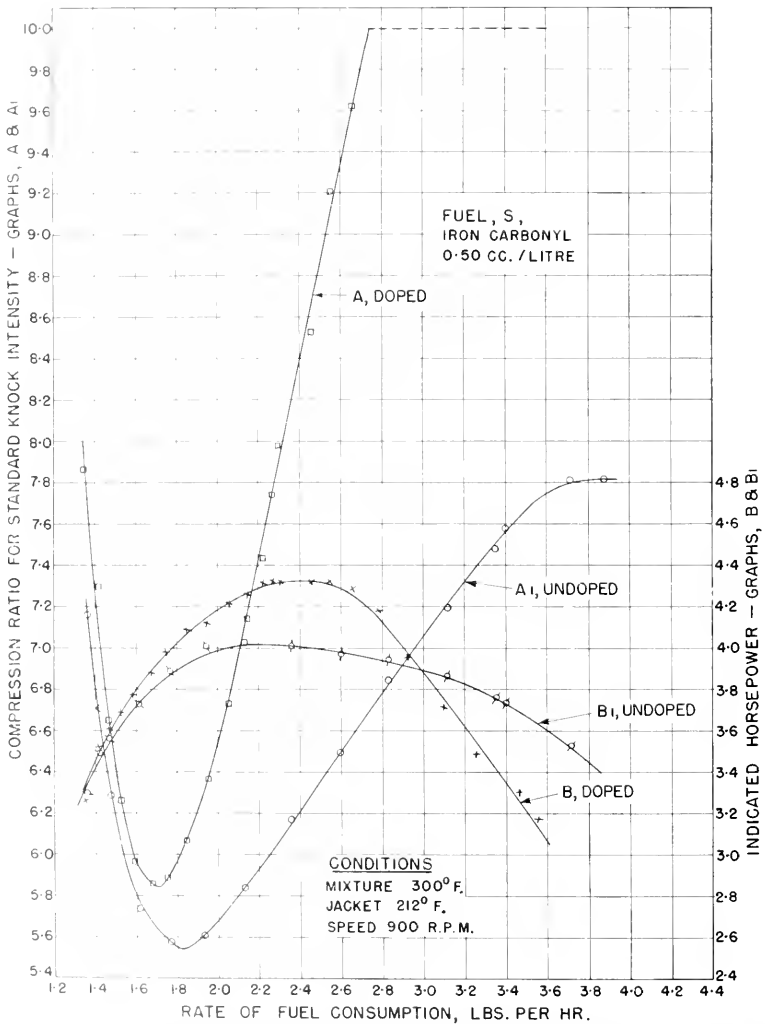


FIG. 5. The relation between usable compression ratio and power as affected by iron carbonyl in the fuel in the concentration of 0.50 cc. per liter.

Concentration: 0.50 cc. per Liter of Iron Carbonyl. Fig. 5

Considering a rate of fuel supply of 1.85 lb. per hr., usable C.R. increased from 5.54 to 6.07 and I.H.P. from 3.93 to 4.07, that is 3.6% on adding the carbonyl.

The maximum I.H.P. of 4.32 for the doped fuel was obtained for a rate of consumption of 2.4 lb. per hr.; the usable C.R. then being 8.4. The I.H.P. for the undoped fuel at the same rate of consumption was 4.0 and the usable compression ratio 6.21. That is, a power increase of 8% only was obtained on increasing the compression ratio from 6.21 to 8.4.

The same I.H.P., namely 3.9, was obtained for both fuels when the rate of consumption was 3.0 lb. per hr. The usable compression ratio for the undoped fuel was then 7.06, while the doped fuel was used at a compression ratio of 10, which is lower than the *usable value which could not be determined* because it exceeded the measurement limit.

Section 2

DISCUSSION OF THE EXPERIMENTAL RESULTS

Little if any adverse effect on power would occur if the temperature required for appreciable surface oxidation were attained late in the combustion period, which generally extends beyond top dead center. The required temperature would not, for example, be expected during compression in an unsupercharged engine at moderate compression ratios with the ingoing mixture raised in temperature solely by the usual induction pipe heating.

It has, however, been shown by laboratory experiments mentioned earlier that a fuel such as pentane doped with iron carbonyl and in rich mixtures with air is oxidized to steam and carbon dioxide with high velocity on surfaces at temperatures as low as 430°C. Higher temperatures would be expected during compression, on surfaces in the cylinders of supercharged aircraft engines, and the experimental results of Section (1) support the view that, even in the C.F.R. engine run in A.S.T.M. knock testing conditions, surface temperatures are high enough to cause preflame oxidation sufficient for an easily measurable adverse effect on power, when rich mixtures containing iron or nickel carbonyl are used.

The adverse effect on power, coincident with the antiknock effect of the metallic dopes in rich mixtures used in the C.F.R. engine, has been calculated from the experimental results of Section (1), see Tables I, II, and III below. The calculations require data for the possible percentage increase in power with increase in compression ratio for a nonknocking fuel used at compression ratios extending to 10. The data given by the graph of Fig. 6 are from those compiled by Pye (14, p. 49) for compression ratios of from 4 to 8, and have been extrapolated to a compression ratio of 10. The assumption is made that percentage increase of power with increase of compression ratio as given by the graph of Fig. 6 can be applied generally.

TABLE I

FUEL S PLUS 0.50 CC. IRON CARBONYL PER LITER

Rate of fuel consumption, lb./hr.	Mixture, per cent rich	Increase of usable C.R.	Observed change of I.H.P.	Percentage increase of I.H.P.	Possible % increase of I.H.P.
2.10	18.8	5.8 to 6.95	4.02 to 4.25	5.72	7.93
2.30	24.3	6.07 to 7.9	4.02 to 4.31	7.2	11.8
2.50	35.0	6.36 to 8.85	4.00 to 4.32	8.0	14.2
2.70	46.0	6.65 to 9.8	3.96 to 4.23	6.8	17.5
3.00	62.0	7.07 to +10	3.90 to 3.90	0.0	15.2+
3.40	84.0	7.57 to +10	3.73 to 3.34	-10.5	12.3+

TABLE II

FUEL S PLUS 0.50 CC. NICKEL CARBONYL PER LITER

Rate of fuel consumption, lb./hr.	Mixture, per cent rich	Increase of usable C.R.	Observed change of I.H.P.	Percentage increase of I.H.P.	Possible % increase of I.H.P.
2.10	18.8	5.81 to 6.27	4.02 to 4.16	3.5	3.5
2.30	24.3	6.07 to 6.81	4.02 to 4.18	3.97	4.73
2.50	35.0	6.35 to 7.37	4.00 to 4.13	3.25	6.63
2.70	46.0	6.65 to 7.90	3.96 to 4.05	2.27	7.87
3.00	62.0	7.07 to 8.50	3.90 to 3.84	-1.54	8.23
3.40	84.0	7.57 to 8.80	3.73 to 3.41	-8.6	6.15

TABLE III

FUEL S PLUS 1.0 CC. NICKEL CARBONYL PER LITER

Rate of fuel consumption, lb./hr.	Mixture, per cent rich	Increase of usable C.R.	Observed change of I.H.P.	Percentage increase of I.H.P.	Possible % increase of I.H.P.
2.10	18.8	5.81 to 6.9	4.02 to 4.27	6.2	6.9
2.30	24.3	6.07 to 7.86	4.02 to 4.33	7.7	11.5
2.50	35.0	6.35 to 8.8	4.00 to 4.34	9.2	14.5
2.70	46.0	6.65 to 9.55	3.96 to 4.27	7.8	16.4
3.00	62.0	7.07 to +10	3.90 to 4.05	3.9	15.2+
3.40	84.0	7.57 to +10	3.73 to 3.43	-8.0	12.3+

Thus, with reference to Table I, for example, maximum power, 4.02 I.H.P., was obtained over the range of mixture strength, 18.8 to 24.3% rich. On adding iron carbonyl in the concentration of 0.50 cc. per liter to the richer mixture, usable C.R. could be raised from 6.07 to 7.9. The corresponding increase in

I.H.P. taken from the experimental results, Fig. 5, was 7.2%. If, however, the fuel had been a nonknocking variety, the increasing of the compression ratio from 6.07 to 7.9 would have resulted in an increase of 11.8% in I.H.P. according to the data of Fig. 6. That is, attainment of the higher usable compression ratio by the use of metallic antiknock was accompanied by a loss of 4.6% of the possible increase in I.H.P.

The power obtainable when using rich mixtures of *undoped* fuel may be affected adversely by the enhanced tendency of such mixtures to oxidize on surfaces in the combustion space of the C.F.R. engine when operated in the high temperature conditions of the A.S.T.M. knock testing method. There-

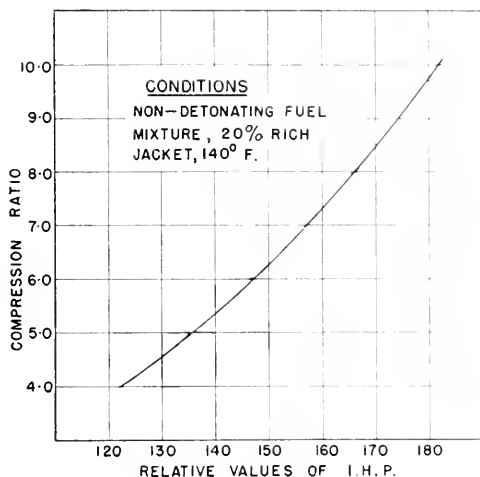


FIG. 6. The relation between compression ratio and power for a nonknocking fuel used in the Ricardo E 35 engine.

fore, the experimental results given in this paper are regarded as representing differences in the adverse effect on power of surface oxidation, between Fuel S and the same fuel containing iron or nickel antiknock.

Mixture strengths given in the tables range from 18.8 to 84% rich. The maximum I.H.P., Fuel S, was constant within the accuracy of measurement over the mixture range 19 to 35% rich and at 84% rich it was 6% only, less than at 2.8% rich. When an engine is run with the compression ratio fixed, it is usually found that power reaches a maximum within the mixture range 10 to 20% rich and diminishes slowly with further increase (13, p. 134). It is to be noted accordingly that values of I.H.P. given in the tables were obtained on increasing compression ratio with increase of mixture strength to maintain a standard knock intensity.

The loss of possible I.H.P. coincident with the antiknock action of the iron and nickel carbonyls is shown by differences between the percentages of Columns 5 and 6 of the tables.

may be seen by reference to Tables I and II that iron carbonyl in the concentration of 0.50 cc. per liter possesses nearly the same antiknock effect as iron carbonyl in double the concentration. It will suffice, therefore, to summarize the principal features of the experimental results obtained when using iron carbonyl.

The possible loss of power coincident with the antiknock action of iron carbonyl in the concentration of 0.50 cc. per liter, Table I, extends from 2 to nearly 11% as mixture strength is increased from 19% to 46% rich. The loss at 62% rich was greater than 15% and at 84% rich it was greater than 22%. The full extent of the losses at mixture strength greater than 46% rich could not be measured because the compression ratio was then off the scale of the engine when the doped fuel was used.

Concluding Comment

The principal interest of the experimental results lies in their confirmation of the theory, advanced in Part III (8), that the metallic antiknocks act by *promoting* the high temperature surface oxidation of hydrocarbon fuel to steam and carbon dioxide, not by inhibiting a homogeneous oxidation reaction by breaking reaction chains.

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THE OXIDATION, IGNITION, AND DETONATION OF FUEL VAPORS AND GASES

XII. THE HIGH COMPRESSION RATIO OTTO CYCLE GAS ENGINE AND THE ADVERSE EFFECT OF HIGH JACKET TEMPERATURES ON THERMAL EFFICIENCY¹

By R. O. KING,² EDWIN J. DURAND,³ AND J. ALEX. MORRISON⁴

Abstract

Town gas was used as the fuel for the C.F.R. engine during a series of engine trials run at a compression ratio of 10 : 1 and at jacket temperatures of 110°, 212°, 302°, and 351° F. The mixture strength at each jacket temperature was varied from the weakest to the richest on which the engine would run steadily. The object of the trials was (1) to determine the effect of jacket temperature on thermal efficiency and (2) to compare the performance of an Otto cycle engine run at 10 : 1 compression ratio with that of a compression ignition (Diesel) oil engine. The results of the trials show that thermal efficiency decreases as the jacket temperature is raised, that is, the decrease more than offsets the gain due to decrease of heat loss during combustion and expansion. It is indicated by the character of the results and by experiments described earlier that the observed loss of efficiency is due to flameless surface combustion of the fuel during compression. The performance of the C.F.R. engine running on town gas at 10 : 1 compression ratio as compared with that of a compression ignition oil engine running at 12 : 1 was superior in respect of maximum power (I.M.E.P.) developed and range of quality control and not greatly inferior in respect of thermal efficiency.

Introduction

It was shown by experiments described in Part VI (3) that town gas, containing hydrogen in large concentration, could be used as fuel for an Otto cycle engine at compression ratios as high as 10 : 1, if precautions were taken to prevent the accumulation in the combustion space of finely divided carbon arising from pyrolysis of the lubricating oil. The power measurements made during the experiments were of a preliminary character but sufficed to show that the increase of compression ratio beyond the 5 : 1 commonly used, made possible by avoidance of nuclear ignition, was accompanied by a commensurate increase in power and thermal efficiency.

The C.F.R. knock testing engine, belt-connected to a d-c. generator, was used for the experiments mentioned. Measurements of power output and friction loss were made consequently by indirect methods and accuracy suffered accordingly. The experimental results of this Part were obtained after a swinging field electric dynamometer had been direct connected to

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and (3) considered that an acceptable accuracy of measurement could be obtained.

The objectives of the experiments were, (1) to determine if flameless surface combustion during compression would more than offset the gain in thermal efficiency due to raising the jacket temperature and (2) to obtain reliable data for an Otto cycle engine running on town gas at a compression ratio of 10 : 1 for a comparison of the performance with that of a compression ignition (Diesel) engine, in respect of power, efficiency, and range of quality control.

Trials were carried out with the jacket coolant at temperatures of 140°, 212°, 302°, and 351° F., mixture strength being varied over the greatest possible range and optimum ignition timing always being used. The temperature of 140° F. can be taken as that of the jacket coolant in motor car engines; 212° F. is the jacket coolant temperature of the A.S.T.M.-C.F.R. method of knock testing; the higher temperatures of 302° and 351° F. represent jacket coolant temperatures of liquid cooled aircraft engines. The cylinders of air cooled engines attain even higher temperatures.

Experimental Arrangements and Results

The C.F.R. engine, which had been used for some weeks for fuel testing, was dismantled and all carbon and other deposits removed from combustion chamber surfaces. The combustion space was maintained sufficiently free of the accumulations of finely divided carbon, which promote pre-ignition and detonation, by the cleaning routine described in Parts V (2) and VI (3).

The valves were refaced and hand lapped into the seats. The piston rings were in good condition and free in the grooves, all of which were clean. The ignition system was checked and the breaker points set to the standard 0.020 in. gap. The spark plug was cleaned and the gap reduced from 0.025 in. to 0.012 in. as had been found necessary in earlier experiments at the high compression ratio of 10 : 1. The setting of the micrometer used for measuring compression ratio was checked, and maximum compression pressures corresponding to compression ratio settings were found to be in agreement with standard C.F.R. values. The maximum compression pressure at 10 : 1 compression ratio was 290 lb. per sq. in., measured during trials at 900 r.p.m. and with the jacket coolant at 212° F.

Lubrication

A commercial grade of lubricating oil, S.A.E. 30, free of additives, was used for engine trials at jacket temperatures of 140° and 212° F. A commercial grade of heavy duty oil, Esso S.A.E. 50, recommended for use with Diesel engines was used for trials made with jacket temperatures of 302° and 351° F.

Jacket Temperatures

The low temperature was obtained by passing tap water through the jacket. The water entered at the lower end of the jacket at 60° F. and flow was

regulated to maintain a nearly constant outlet temperature of 140° F. The standard evaporative method of cooling, using water, was employed to obtain a jacket temperature of 212° F. The higher jacket temperatures of 302° and 351° were obtained by evaporative cooling, using ethylene glycol suitably diluted with water, an extra section being fitted to the reflux condenser.

Power Measurement

The belt driven main and auxiliary generators of the C.F.R. unit were disconnected from the engine. The main generator was then driven as a motor from the laboratory d-c. supply and it in turn drove the auxiliary generator which supplies current for engine auxiliaries, such as the bouncing pin and the ignition system. The engine was then direct connected to a d-c. swinging field dynamometer with beam type scale. Thus, brake horsepower was measured. Indicated horsepower was obtained by adding to the observed B.H.P. that required to overcome friction and pumping losses when fuel was not added to the air supply and the engine "motored" by the dynamometer. "Motoring" loss was measured after every set of power observations as soon as possible after stopping the fuel supply. A set of observations comprised 6 power measurements made to determine optimum ignition timing for any particular rate of gas supply (mixture strength). Average values of the horsepower absorbed by friction and pumping losses, described hereafter as L.H.P., were as below,—

140° F. jacket, S.A.E. 30 oil	—1.45 L.H.P.
212° F. jacket, S.A.E. 30 oil	—1.31 "
300° F. jacket, S.A.E. 50 oil	—1.24 "
350° F. jacket, S.A.E. 50 oil	—1.17 "

The relatively great loss at 140° F. jacket temperature is due to the entrance of tap water into the lower end of the cylinder jacket at 60° F.

Measurement of Rate of Gas Consumption

Measurements were made by members of the technical staff of the Consumers' Gas Company of Toronto, using a standard dry meter especially fitted and calibrated for accurate measurement.

Calorific Value of the Town Gas

The composition and calorific value of Toronto town gas are closely controlled. The composition remained constant during the engine trials at jacket temperatures of 212° F. and higher, made on successive days, but differed slightly from that during the trial at 140° F. jacket temperature made some weeks earlier, as shown by the data of Table I.

The higher calorific value of the gas used for the trial at 140° F. jacket temperature, determined by calorimeter in the Gas Company laboratory, was 465.1 B.t.u. per cu. ft. and the corresponding lower calorific value obtained by calculation was 422.2 B.t.u. per cu. ft. Values obtained similarly for the gas when used later at the higher jacket temperatures were 470 and 427

TABLE I
COMPOSITION OF TORONTO TOWN GAS AT TIMES OF ENGINE TRIALS;
PERCENTAGE VOLUMES

Constituents	Trial at 140° F., jacket temperature	Trials at higher jacket temperatures
Hydrogen	48.3	47.4
Carbon monoxide	23.3	21.7
Methane	11.0	12.4
Nitrogen	7.1	7.6
Carbon dioxide	3.7	4.2
Ethylene	3.0	3.8
Ethane	1.8	1.3
Benzene	1.1	0.9
Oxygen	0.8	0.7

B.t.u. per cu. ft. The "lower" values were used for calculating indicated thermal efficiency. All are for the gas at 60° F. and 30 in. of mercury.

Carburetor Arrangement

The method of admitting gas to the C.F.R. carburetor as used in preliminary experiments is shown by Fig. 1 of Part VI (3). The open end of the gas admission tube was fully exposed to the air oscillations in the induction system of the engine. The oscillations were probably without effect on the accuracy of the gas meter, but as a precaution the open end of the tube was closed and the gas passed through three rings of small holes in the wall of the tube. The air heater of the C.F.R. engine was left in place and provided a mixing chamber for the gas and air.

Ignition Timing for Maximum Power

The required ignition timing at constant engine speed and compression ratio varies with jacket temperature and mixture strength. Air and gas were both supplied to the engine at atmospheric pressure. The ignition advance required for the maximum power obtainable for a particular rate of gas consumption can be determined only by experiment. Thus the brake horsepower developed when a particular mixture was used was measured at a series of ignition timings giving rising and falling power. The optimum timing was then obtained from a plot of the results.

The method is illustrated by the graphs of Fig. 1, plotted to determine the optimum ignition timing for 14 rates of gas consumption ranging from that required for the weakest to the richest mixtures on which the engine would run steadily. It will be seen by reference to the graphs that optimum ignition timing varies over a wide range, and is somewhat sharply defined at any particular mixture strength. Thus at the weakest mixture on which the engine would run continuously, given by a rate of gas consumption of 47.5 cu. ft. per hr., optimum timing was 44° advance and output was 1.92 B.H.P. The maximum power output of 4.06 B.H.P. was obtained at a rate of gas consumption of 92.5 cu. ft. per hr., and optimum ignition timing was then 13.5° advance. The graphs for mixtures richer than that required for maxi-

imum power are given separately in the right hand top corner of Fig. 1 to save confusion. They show, as usually found, that optimum ignition timing varies less with mixture strength on the rich than on the weak side of the maximum power mixture strength.

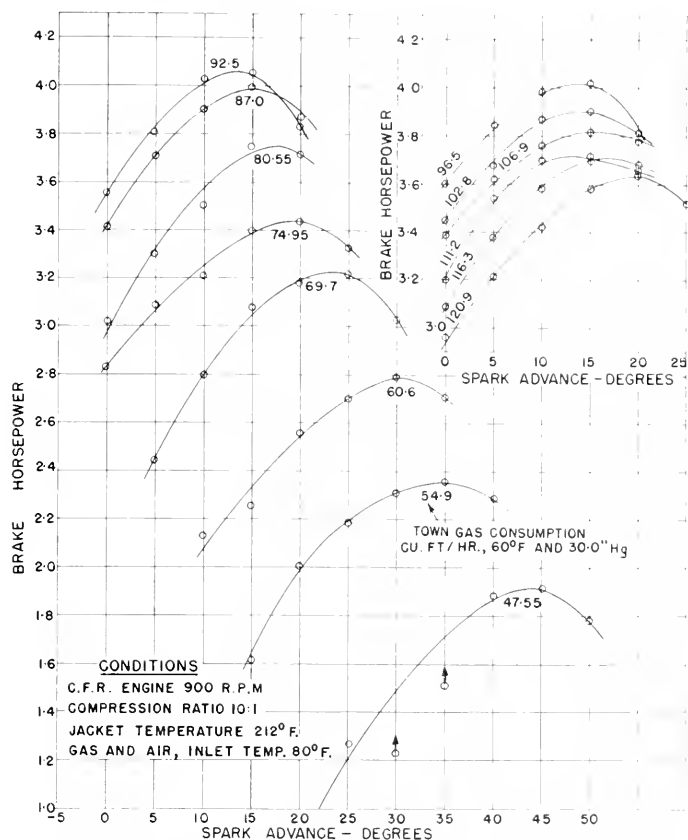


FIG. 1. Graphs for the determination of optimum ignition timing for each of the 14 rate of gas consumption required for the set of trials made at a jacket coolant temperature of 212° F.

The experimental results required for the graphs of Fig. 1 were obtained when the jacket coolant temperature was 212° F. Similar sets of graphs were obtained for jacket coolant temperatures of 302° and 351° F. and for a jacket coolant temperature (outlet) of 140° F.

Brake and Indicated Horsepower, Mechanical Efficiency, 212° F. Jacket Coolant Temperature, Optimum Spark Advance

The experimental results given by the graphs of Fig. 1 were used to plot the graphs of Fig. 2. Graph A of the figure gives the relation between optimum spark advance and rate of gas consumption and Graph B the corresponding brake horsepower. Graph C, for indicated horsepower, represents the brake horsepower plus the horsepower (L.H.P.) lost in overcoming mechan-

and fluid friction, amounting to 1.31 B.H.P. at the jacket coolant temperature of 212 F. Graph *D*, for mechanical efficiency, gives the percentage relation of brake to indicated horsepower. It will be noted that the value at maximum power output is approximately 76%, a reasonable value in view of the engine's not having been designed for high output and low friction loss.

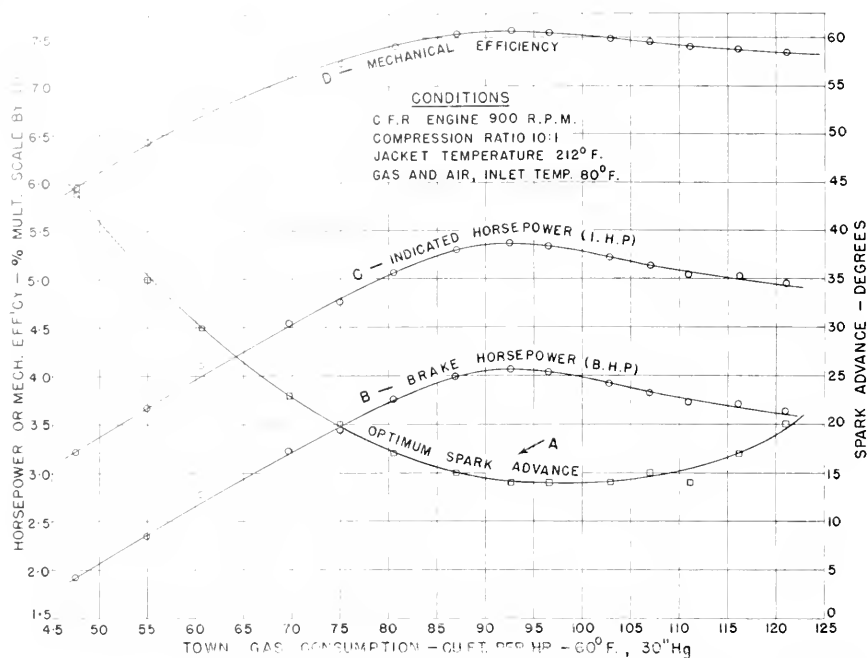


FIG. 2. Mechanical efficiency and brake and indicated horsepower at optimum spark advance—jacket coolant, 212° F.

Indicated or brake mean effective pressures can be obtained by multiplying values given by Graphs *C* and *B* by the factor 23.4. Thus I.M.E.P. at maximum power output was 125 lb. per sq. in.

Indicated Thermal Efficiency and Power

The internal combustion engine, being noncondensing, is restricted to converting into work some part only of the "lower" heat value of the fuel used. It is necessary therefore to use that value for calculations of thermal efficiency if comparable results for a variety of fuels are to be obtained, because the difference between the lower and higher values varies with the nature of the fuel.

Similarly, when the efficiencies of a variety of engines are compared it is necessary to take into account the total power developed, because the fraction used in overcoming friction varies with design and operating conditions. The total is represented by the indicated horsepower or by the indicated mean effective pressure.

Thus, considering as an example a particular set of engine trials at 900 r.p.m., the jacket coolant at 212° F. and compression ratio 10 : 1, the data used for the calculation of indicated thermal efficiency were as follows:

Metered rate of gas consumption, 96.6 cu. ft. per hr.

Lower calorific value of the gas at 60° F. (520° R.) and 30 in. of mercury barometric pressure, 122 B.t.u. per cu. ft.

Gas temperature at meter, 73.7° F. (533.7° R.)

Barometric pressure, corrected for temperature, 29.33 in. of mercury

Brake horsepower by dynamometer, 1.06

Friction horsepower (L.H.P.) by dynamometer, 1.31

Indicated horsepower by addition, 5.37

The rate of heat input to the engine is then,

$$422 \times \frac{520}{533} \times \frac{29.3}{30.0} \times \frac{96.6}{60} = 646 \text{ B.t.u. per min.}$$

and the equivalent ft. lb. per min. = 646×778

The rate at which heat is converted into work is

L.H.P. (5.37) \times 33000, ft. lb. per min.

and per cent indicated thermal efficiency

$$= 100 \times \frac{5.37 \times 33000}{646 \times 778} = 35.2$$

COLLECTED RESULTS OF ENGINE TRIALS

The results of trials made with a jacket coolant temperature of 212° F. are given by the graphs of Fig. 3. They are plotted on a brake horsepower base extending from the minimum power at which the engine would run steadily to the maximum power that the engine would develop. The obtainable range of B.H.P. is shown by the vertical broken lines. It will be noted that power reaches a maximum for a particular rate of gas consumption and then diminishes as the rate is further increased. Thus the familiar consumption "loop" is obtained.

Indicated thermal efficiency attains relatively high values at weak mixtures, decreases slowly until the mixture strength for maximum power is reached, and then very rapidly with further increase in mixture strength. Then as power decreases at the same time, an indicated thermal efficiency "loop", as shown by the relevant graph of the figure, is obtained.

The results of trials made with a jacket temperature of 351° F. are presented similarly by the graphs of Fig. 4. The similar graphs for trials made at 140° and 302° F. are not reproduced because of space limitation.

The features of special interest in respect of the trials made at the four jacket coolant temperatures of the experiments are exhibited by the graphs of Fig. 5. The *A* graphs are consumption loops, and *B* graphs indicated thermal efficiency loops. They show in a striking way the progressive de-

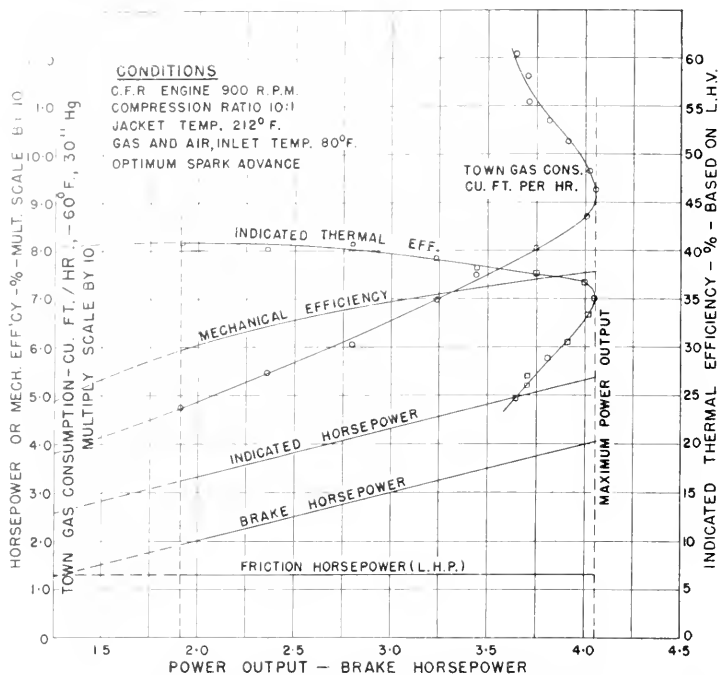


FIG. 3. Graphical presentation of the results of trials made with the jacket coolant at 212° F.

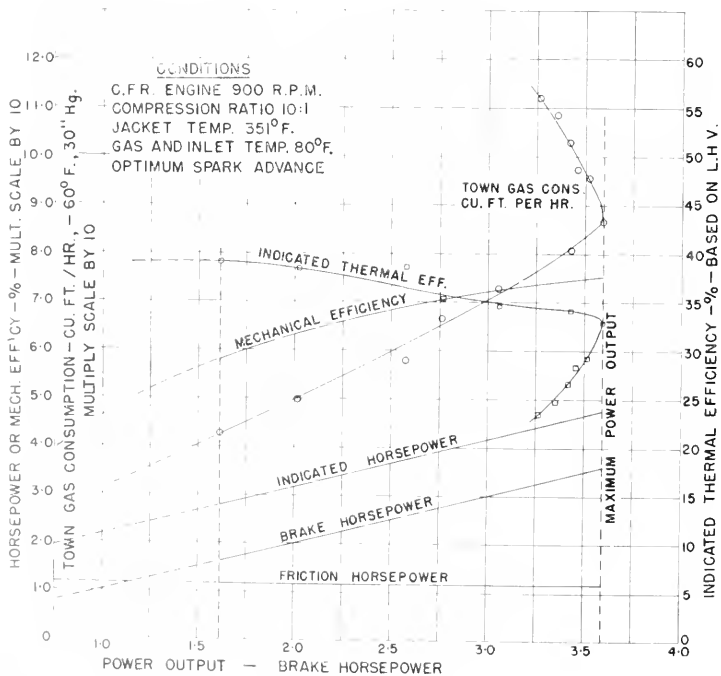


FIG. 4. Graphical presentation of the results of trials made with the jacket coolant at 351° F.

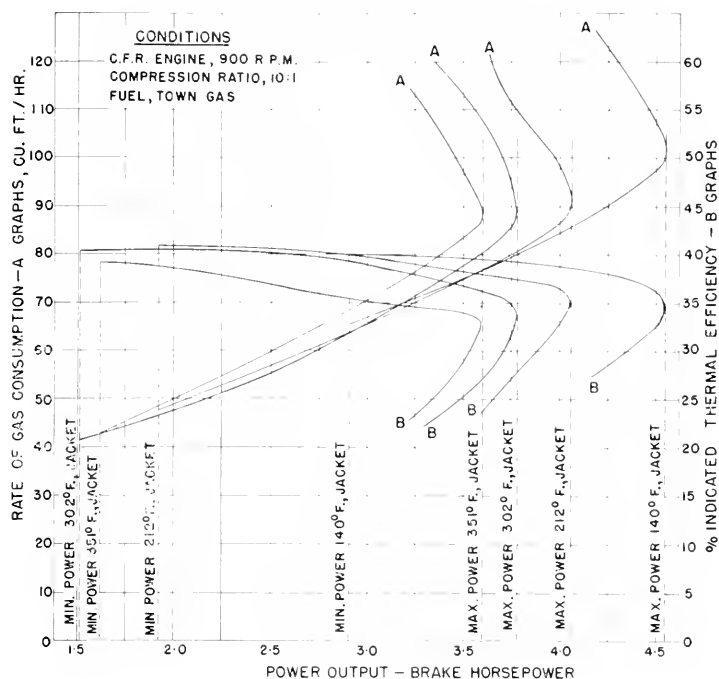


FIG. 5. Consumption loops given by A graphs and indicated thermal efficiency loops by B graphs; for trials made with jacket coolant temperatures of 140°, 212°, 302°, and 351° F.

crease of indicated thermal efficiency and power as jacket coolant temperature is raised from 140° to 351° F. Maximum and minimum powers obtained for each jacket coolant temperature are shown by the vertical broken lines. It will be noted that a relatively high value of minimum power was obtained when the jacket coolant temperature was 140° F. This anomalous result is thought to be due to ignition failure at weaker mixtures.

Summary and Discussion of Experimental Results

It was not considered possible, prior to the experiments described in Parts V (2) and VI (3), to operate an Otto cycle engine on hydrogen or town gas at a compression ratio of 10:1, except when using weak mixtures and consequently obtaining relatively low values of mean effective pressure. Thus, there are not extant any engine trial results for Otto cycle engines with which the experimental results given in this Part can be compared. Recourse must therefore be to the trial results of the compression ignition type of the Diesel engine. The most comprehensive described trials of that type of engine are, so far as known, those by H. B. Taylor (8, pp. 35-85). Data are given for trials run at 12:1 compression ratio and speeds of 800 and 1000 r.p.m. and with injection timing fixed or advanced progressively with decrease in mixture

strength. A comparison of the C.F.R. Otto cycle engine trial results with those given by Ricardo (6) for the compression ignition engine are therefore of interest although weighted in favor of the latter by the higher compression ratio of 12:1 at which they were run. The temperature of the jacket coolant is not mentioned in Taylor's paper but can be assumed to have been that generally used, namely, 60° C. (140° F.).

Thermal Efficiency as Affected by Jacket Temperature

An increase in jacket temperature, by diminishing heat loss during the combustion and expansion periods, should give rise to a small increase in thermal efficiency. The possibility that the increase might be more than offset by the adverse effect of surface oxidation of the fuel has not heretofore been considered, the established (textbook) view being that "no significant surface reaction occurs in the engine" (1, p. 2934).

The adverse effect of flameless surface combustion on the power developed by an Otto cycle engine running on gasoline was shown by the experiments described in Part XI (4). The experiments of this Part were made to determine if a similar effect would be obtained in suitable conditions if the engine were run on town gas containing a large proportion of hydrogen, which reacts with metallic oxide at relatively low temperatures to form steam. The experimental results obtained accordingly are summarized in Table II. The data given for jacket coolant temperatures of 212° F. are from the graphs of Figs. 2 and 3. The data relating to other jacket coolant temperatures are from similar graphs, which are not reproduced because of space limitations.

TABLE II

INDICATED THERMAL EFFICIENCY AND INDICATED MEAN EFFECTIVE PRESSURE
AS AFFECTED BY JACKET COOLANT TEMPERATURE

Jacket coolant temperature, F.	Max. power		75% max. power		Min. power	
	I.M.E.P., lb./sq. in.	I.T.E., %	I.M.E.P., lb./sq. in.	I.T.E., %	I.M.E.P., lb./sq. in.	I.T.E., %
140	140.4	35	105	40	(102)	(40)
212	125.0	35	94	40	76	41
302	117.0	33.5	88	40	65	40
351	111.0	32.5	83	37	65	39

With reference to Table II, consider first the effect on thermal efficiency of raising the jacket temperature from 140° to 212° F. The estimates by Ricardo (6, p. 87) and Ricardo and Glyde (7, p. 103), which are not based on experiment, led to the conclusion that an increase of from 0.4% to 1.0% would be obtained. This no doubt is an accurate estimate, taking into account heat loss only. The *experimental* results given in Table II show, however, that no change in thermal efficiency occurred within the jacket coolant temperature range 140° to 212° F., the minimum power measurements at 140° F. being disregarded, for the reason already mentioned. It may be

concluded accordingly that the gain due to the lower heat loss during combustion and expansion was just equal to the loss due to surface oxidation of the fuel during compression.

Consider now the effect on efficiency of raising the jacket coolant temperature from 212° to 351° F. There should, of course, be a gain in thermal efficiency due to lower heat loss to the jacket but instead efficiency decreases by 7% at maximum power and by 7½% at three-quarter power. The total loss attributable to surface oxidation would therefore be the sum of the percentages mentioned plus whatever gain there might have been, taking into account the lower heat loss to the jacket.

The smaller efficiency loss of 1.9%, observed when using the weak mixture required for minimum power, is attributed to the decrease in velocity of the surface reaction with decrease in mixture strength.

Thermal Efficiency, Weak Mixtures

Thermal efficiency should, according to generally accepted theory, approach the Air Standard value as the concentration of fuel in the mixture with air approaches zero. The experimental results obtained with the C.F.R. engine running at 10 : 1 compression ratio indicate, on the contrary, that thermal efficiency attains a maximum value at a mixture strength richer than the weakest on which the engine continues to run. A similar effect was obtained as a result of earlier experiments with town gas [Part VI (3)]. The observed decreases from the maximum, although small, are of sufficient interest to justify further experiments.

Quality Control

A feature of the Diesel or compression ignition type of Diesel is that power output at any particular speed can be varied over a wide range by varying the rate of fuel supply, that is, the "quality" of the fuel-air mixture. It became of interest, therefore, to determine the degree of quality control obtained when the C.F.R. engine was run at 10 : 1 compression ratio and with jacket coolant temperature varied over a wide range.

Percentage quality control is taken to be:—

$$\frac{\text{Maximum B.H.P.} - \text{Minimum B.H.P.}}{\text{Maximum B.H.P.}} \times 100$$

Relevant data from the C.F.R. engine experiments are set out in Table III.

TABLE III
QUALITY CONTROL DATA, C.F.R. ENGINE
10 : 1 COMPRESSION RATIO

Temperature of jacket coolant, ° F.	Max. B.H.P.	Min. B.H.P.	Friction H.P.	Percent Q control
140	4.55	2.91	1.35	36
212	4.05	1.91	1.31	53
302	3.76	1.52	1.24	60
351	3.60	1.61	1.17	55

The relatively low percentage quality control at 140° F. jacket coolant temperature is believed to be due to ignition failure, as already mentioned.

The obtaining of a wide range of quality control depends on continuing ignition as mixture strength is progressively weakened. The spark ignition system of the C.F.R. engine is not especially adapted for use with very weak mixtures, and although the results are somewhat irregular, as would be expected, it is of interest to compare them with those relating to compression ignition engines as given by Taylor (8).

The percentage quality control obtainable with the compression ignition engine was found by Taylor (8) to diminish with speed and to be little affected by injection timing. Relevant data, taken from page 47 of the reference quoted, are given in Table IV.

TABLE IV
QUALITY CONTROL DATA, COMPRESSION IGNITION ENGINE,
12 : 1 COMPRESSION RATIO

Engine r.p.m.	Max. B.H.P.	Injection degrees advance	Min. B.H.P.	Injection advance	Percent Q control
800	64.6	11.5	30		54
800	65.0	12.5	30	31.5	54
1000	80.0	12.0	40		50
1000	79.5	12.0	40	29.5	50

The percentage quality control for the compression ignition engine if run at 900 r.p.m. can be taken as 52. The Otto cycle C.F.R. engine run at that speed and at the lower compression ratio of 10 : 1 affords quality control of 53, 60, and 55% for jacket temperatures of 212°, 302°, and 351° F. respectively.

Quality control is determined by the spread between maximum and minimum brake horsepower (B.M.E.P.). The minimum cannot be greater than the B.H.P. required to overcome friction and pumping losses and may be more nearly reached with the Otto cycle engine by improving spark ignition at weak mixtures. The maximum can be the greater for the Otto cycle engine because of the inability of the compression ignition engine effectively to utilize the mixture strength required for maximum power.

Volumetric Efficiency, Spark Advance

The engine was always run at constant speed and compression ratio, and any decrease in volumetric efficiency observed on raising the jacket temperature would be due to the consequent heating of the induced charge. The extent of the decrease for a particular increase of jacket temperature would depend mainly on the turbulence and thermal conductivity of the gas-air mixture entering the cylinder. The mixture enters the cylinder of the C.F.R. with a high degree of turbulence because of high velocity attained in passing through a somewhat restricted inlet valve opening, and the gas-air mixture

containing hydrogen in large proportion is of relatively high thermal conductivity. The conditions of the engine trials were therefore such that a large decrease in volumetric efficiency would be expected. Moreover, the increase in charge temperature due to increasing the jacket temperature would give rise to an increase in compression temperature, a corresponding increase in rate of flame propagation after spark ignition, and a consequent decrease in optimum spark advance. Relevant data collected from the experimental results are set out in Table V.

TABLE V
EFFECT OF JACKET TEMPERATURE ON VOLUMETRIC
EFFICIENCY AND OPTIMUM SPARK ADVANCE

Jacket coolant temperature, ° F.	Maximum I.H.P.	Gas consumption cu. ft. hr.	Spark advance
140	6.00	102	16°
212	5.40	91.5	14°
302	5.00	88.5	8°
351	4.75	87	4°

When the engine charge is heated during induction, volumetric efficiency diminishes and indicated power decreases in the same proportion if speed and compression ratio remain constant, according to a discussion by Pye (5, p. 240), of experiments by Ricardo. On this basis the decrease of maximum I.H.P. from 6.00 to 4.75, Table V, indicates a large decrease of 20.8% in volumetric efficiency. The method of calculation is based necessarily on the generally accepted view that indicated thermal efficiency does not *diminish* with increase of jacket temperature. It has been shown, however, Table II, that a decrease of 7% was obtained on increasing jacket coolant temperature from 140° to 351° F. Thus of the total decrease of 20.8% in I.H.P., 13.8% represents that due to decrease of volumetric efficiency.

The change in volumetric efficiency can be calculated by another method. Thus, when the engine charge is gas and air, both being supplied at the same temperature and pressure, the rate of consumption of either is proportional to volumetric efficiency *if mixture strength remain constant*. It may safely be assumed that the mixture strength for maximum power is invariable. With reference to Table V, rate of gas consumption at maximum power diminishes from 102 to 87 cu. ft. per hr., that is, by 14.7% when the jacket coolant temperature is raised from 140° to 351° F. The decrease in volumetric efficiency of 14.7% agrees as well as could be expected with the value of 13.8% deduced from observed changes in power and efficiency.

Optimum Ignition Timing

The decrease in optimum spark advance as jacket temperature is raised is given in Table V and reflects the increase in rate of flame propagation as compression temperature increases with increase in the temperature of the gas-air mixture at the beginning of compression. The result, so far as engine

operation is concerned, is that the usual effects of excessive spark advance, namely, loss of power accompanied by rough running and knock, are obtained for a relatively small advance beyond the optimum value.

Concluding Comment

The Adverse Effect of Surface Combustion on Thermal Efficiency

The decrease of thermal efficiency obtained on raising the temperature of the jacket coolant of the C.F.R. engine is attributed to the effect of flameless combustion of hydrogen on oxide coated surfaces, to produce steam during compression. The decrease of efficiency becomes greater as mixture strength increases because the velocity of the surface reaction increases accordingly. Thus the decrease in indicated thermal efficiency, Table II, is 7% at the mixture strength for maximum power. It is 10.3%, that is, 50% greater for the richer mixture obtained on increasing rate of gas consumption by 20%. The adverse effect on thermal efficiency due to surface oxidation is similar to that described in Part XI (4), obtained when surface oxidation of liquid fuel vapor to steam and carbon dioxide occurred on a metal surface maintained in an oxidizing atmosphere by continuous decomposition of a metallic antiknock.

It is to be noted that the conclusion in respect of the cause of the decrease in thermal efficiency with increase in jacket temperature is based on the somewhat indirect evidence afforded by earlier experiments, mainly those described in Part XI (4). Further experiments made in a manner to eliminate surface combustion would therefore be of interest.

Otto Cycle Compared with Compression Ignition (Diesel) Performance

Combustion in the compression ignition (C.I.) engine leaves unused from 20 to 25% of the air in the cylinder charge. This is approximately the percentage of the air displaced when town gas in "correct" proportion with air is used as the fuel for an Otto cycle engine. Combustion of the fuel, especially when rich mixtures are used, is the more nearly complete in the Otto cycle engine because of the homogeneity of the mixture with air. It would be of interest to compare performances on the basis of the same compression being used. A comparison can however be made at present on the basis of 10:1 compression ratio only and 900 r.p.m. for the C.F.R. Otto cycle engine and 12:1 compression ratio and 1000 r.p.m. for the C.I. engine. The data for the "best" performance of the C.I. engine used by Taylor (8) are given (page 47 of the reference). The maximum cylinder pressure was 800 lb. per sq. in. and injection timing was advanced as load was reduced.

The maximum I.M.E.P. obtained by Taylor was 133.7 lb. per sq. in., with an indicated thermal efficiency of 38.3%. The corresponding figures for the C.F.R. Otto cycle engine were 140.4 and 35%.

The I.M.E.P. obtained by Taylor at the weakest usable mixture strength was 77.5 lb. per sq. in. with an indicated thermal efficiency of 46.4%. The

corresponding figures for the C.F.R. engine were (at 212° F. jacket temperature) 76 lb. and 41%.

The C.F.R. Otto cycle engine was somewhat superior in respect of the important feature of quality control, as shown by the data of Tables III and IV.

Acknowledgments

The experimental work was carried out with the co-operation of Prof. E. A. Allcut, Head of the Department of Mechanical Engineering, University of Toronto, and Assistant Professor W. A. Wallace. Special acknowledgment is made of the assistance of Mr. George Southall of the laboratory staff of the Consumers' Gas Company, who carried out the long series of gas supply measurements. Assistance was also given in the course of the experiments by Messrs. C. C. Li, E. H. Dudgeon, W. E. Morley, and H. W. M. Mar, all members of the staff of the Department of Mechanical Engineering.

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THE OXIDATION, IGNITION, AND DETONATION OF FUEL
VAPORS AND GASES

XIII. THE 12 : 1 COMPRESSION RATIO PERFORMANCE OF THE C.F.R.
SPARK IGNITION ENGINE USING TOWN GAS; COMPARISON
WITH DIESEL ENGINES

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BY R. O. KING², E. J. DURAND³, BERNARD D. WOOD⁴,
AND A. B. ALLAN⁵

Abstract

The experiments described are part of a series being made to determine the factors which limit the power and efficiency of an Otto cycle spark ignition engine using Toronto town gas nearly free of sulphur. The air supply was unthrottled and power was varied by varying the gas supply. Mixture strength was "correct" at an air-to-gas ratio of 14:1. Trials were run with jacket coolant temperatures of 100°, 140°, 212°, and 295° F., the compression ratio being always 12:1 and the speed 900 r.p.m. A maximum indicated thermal efficiency of 43% was attained with coolant temperatures of 100° and 140° F. and an air-to-gas ratio of 8:1. Thermal efficiency diminished rapidly as air-to-gas ratio was increased and tended to become zero instead of the air standard value. The brake horsepower became zero for an air-gas ratio of approximately 11:1, the mixture strength being then 64% weak. Thus the engine was run at 900 r.p.m. from zero to full load, that is with 100% quality control. The maximum I.M.E.P. of 144 lb./sq. in. was obtained with a jacket coolant temperature of 100° F. The indicated thermal efficiency was then 36% and the mixture 10.7% rich. The performance of the Otto cycle engine could probably be improved by running at higher speeds but even at the relatively low speed of 900 r.p.m. for that type, it compared favorably in most respects with that of the compression ignition type of Diesel engine.

Introduction

It was shown by the preliminary experiments described in Part VI (7) that town gas containing hydrogen in the relatively large proportion of nearly 50% could be used as the sole fuel for a spark ignition Otto cycle engine at 10:1 compression ratio, if nuclear ignition were avoided. A comprehensive series of trials was carried out later at the same compression ratio, to determine the effect of jacket temperature on thermal efficiency, Part XII (5). Power and efficiency were not limited by the onset of detonation even when the temperature of the jacket coolant was 351° F. A compression ratio of 10:1 had currently been regarded as impossibly high for town gas, and consequently there were no published experimental results available for discussion of the observed performance relative to that obtained by others with the same type of engine.

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It was necessary, therefore, to use compression ignition (Diesel) engine performance as a basis of comparison and 12 : 1 was the lowest compression ratio for which the results of comprehensive compression ignition engine trials were available. Even so, the performance of the spark ignition engine on town gas at 10 : 1 compression ratio did not compare altogether unfavorably with that of a compression ignition oil engine at 12 : 1 compression ratio, (5 p. 448).

Spark ignition engine trials made when using Toronto town gas at a compression ratio of 12 : 1 and jacket coolant temperatures of from 100° to 295° F. are described in this Part. An improved ignition system was used and air-gas ratios were determined by measurement of the rates of supply of both gas and air.

The engine trials are part of a continuing investigation of the factors which limit the power and thermal efficiency of the internal combustion engine.

Experimental Arrangements and Results

THE ENGINE

The C.F.R. knock testing engine used for the trials was "standard" except that, as for experiments described in earlier Parts, the shrouded inlet valve was replaced by one of the common type. The compression ratio of 10 : 1, usually regarded as the maximum available, is limited to that value by the one inch range of the micrometer used for the measurement of the setting of the movable cylinder head and the consequent compression ratio. The measurement limit was extended to provide for compression ratios of 12 : 1 and higher by using a distance piece of accurately known length to raise the spring loaded micrometer spindle accordingly.

The engine was prepared for the trials by being dismantled for the removal of all carbon and other deposits from the combustion chamber and piston ring grooves. The rings were found to be in good condition. The valves were cleaned and hand lapped into the seats. The combustion space was maintained, during the trials, as nearly free of loose carbon as was possible by daily cleaning with a brush and scraper, inserted into the combustion space through the spark plug and bouncing pin openings.

The maximum compression pressure at 12 : 1 compression ratio as measured by a Keine Gage was 390 lb. per sq. in. gauge at 900 r.p.m., 68° F. inlet air temperature, 29.9 in. of mercury atmospheric pressure, and jacket coolant, 212° F. All trials were made without throttle control.

Lubrication, as in earlier trials, was with a commercial grade of oil, S.A.E. 30, free of additive, for jacket coolant temperatures of 212° F. and lower. Similar lubricating oil but S.A.E. 50 viscosity grade was used for trials at 295° F. coolant temperature.

THE IGNITION SYSTEM

It was found, during the engine trials with hydrogen, Part V (6), and town gas, Part VI (7), that the ignition system supplied as standard with the C.F.R. knock testing engine was ineffective at a compression ratio of 10 : 1 unless the spark gap were reduced from the standard 0.025 in. to 0.012 in. The narrower gap was used for the trials of Part XII (5) and it was surmised that the ignition failure observed at very weak mixtures might thus be explained. The ignition system of the engine was revised in accordance with suggestions by C. Cipriani (2) and it then became possible when using a spark gap of 0.020 in. to ignite the extremely weak mixtures required for zero brake horsepower at a compression ratio of 12 : 1 and to obtain 100% quality control accordingly. The revised ignition system is described in Section (a) of the Appendix.

JACKET COOLANT TEMPERATURE

The method of evaporative cooling in conjunction with a reflux condenser used as standard for the C.F.R. engine provides coolant temperatures of nearly 212° F. when water is used and higher temperatures on adding ethylene glycol to the water, the high limit being 375° F., the boiling point of the glycol. The method has the special advantage that the coolant remains at a substantially constant temperature from the inlet at the lower end of the cylinder barrel jacket to the outlet at the top of the combustion chamber jacket. The method was found to be difficult of application if used to obtain coolant temperatures lower than 212° F. in part because of the relatively low specific heats of liquids having suitable boiling points and the consequently required increase in the capacity of the reflux condenser.

Jacket coolant temperatures lower than 212° F. when required for the experiments described in earlier Parts were obtained by using cold tap water. The outlet temperature could then be varied by regulating the rate of water flow but it was not that of the coolant surrounding the whole of the combustion chamber and the cylinder barrel, and the large temperature gradient along the cylinder barrel was accompanied by obviously objectionable conditions of lubrication.

It seemed to be possible to improve on conventional cooling methods by using a thermostatically controlled hot and cold water blender, automatically to maintain a coolant temperature nearly uniform from the inlet to the outlet of the engine jacket. The cooling method designed accordingly is described in Section (b) of the Appendix. It was used for experiments described in this Part to provide jacket coolant temperatures of 100° F. and 140° F. with a temperature change of not more than 6° F. between jacket inlet and outlet.

MIXTURE STRENGTH MEASUREMENT

When using paraffinic fuels which have a definite tendency to detonate, mixture strength can be taken as approximately "correct" at the rate of fuel supply giving maximum knock and mixture strength at other rates of fuel supply, estimated accordingly. When nondetonating fuels such as hydrogen or town gas are used, the sole reference point is the mixture strength for maximum power, and it does not bear any certain relation to the "correct" value. Measurements of rates of supply of both air and gas, as required for determinations of mixture strength, were carried out during the trials described in this Part. A standard dry meter especially fitted and calibrated for accurate measurements was supplied by the Consumers' Gas Company for measurement of the rate of gas supply to the engine. A special arrangement of the air-box orifice method was used for metering the air supply. It is described in Section (c) of the Appendix.

THE FUEL GAS

Toronto town gas was used for all the C.F.R. engine trials of this Part. An average percentage by volume composition is: hydrogen, 48; carbon monoxide, 22; methane, 12; other hydrocarbons, 6; nitrogen and carbon dioxide, 12. The gas contains sulphur in the organic form only, in extremely small concentration varying from 10 to 15 grains per 100 cu. ft. as compared with the 30 grains permitted by many municipal and state authorities. The composition of the gas varies slightly from time to time. Determinations of composition and calorific value are made continuously, and the values at the times of engine trials were given by the Consumers' Gas Company.

IGNITION TIMING

The trials were made at constant compression ratio and engine speed. Optimum ignition timing taken as the spark advance required for the development of maximum brake horsepower was dependent, therefore, on mixture strength and to some extent on jacket temperature. Mixture strength was varied during any trial made at a particular jacket temperature, over the widest practicable range. Eighteen mixture strength settings were used for every one of the trials made at the four jacket temperatures. The spark advance required to provide optimum ignition timing in all cases was determined by the method described in Part XII (5, pp. 438-39). The application of the method to the trials of this Part required a determination of the relation between power and spark advance and a plot of the results for the 18 values of mixture strength used for each of the four jacket temperatures. The optimum spark advance determined accordingly to provide for all conditions of the trials is given by related trial result graphs. It is not considered necessary to display the 72 graphs on which values are based.

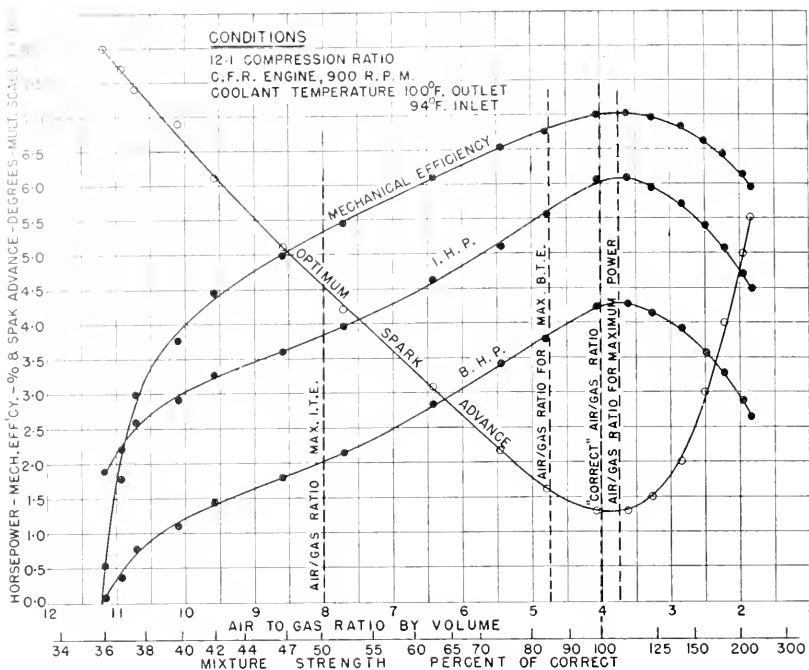


FIG. 1. Engine trial, jacket coolant 100° F. showing variation of power, optimum spark advance and mechanical efficiency with air-to-gas ratio and mixture strength.

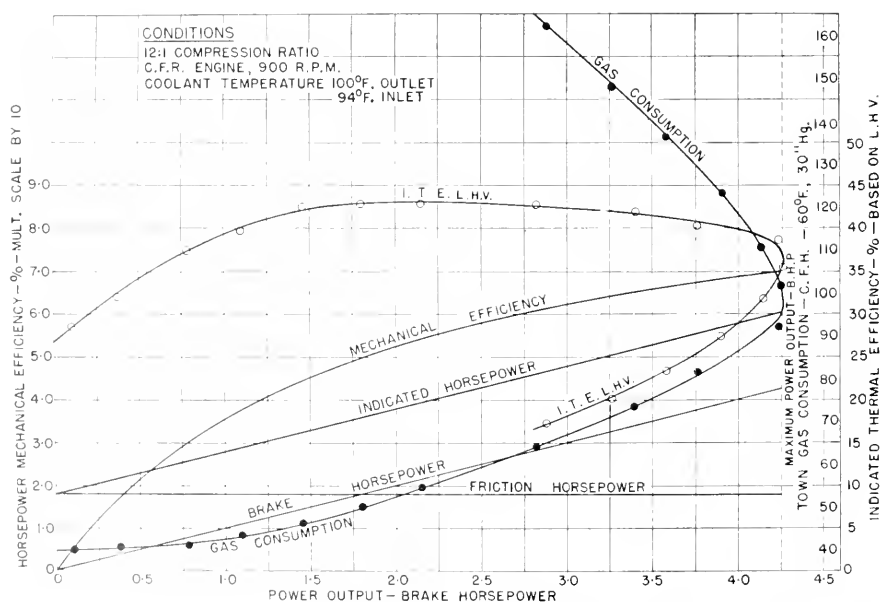


FIG. 1A. Engine trial, jacket coolant 100° F. showing variation of indicated thermal efficiency, mechanical efficiency, and gas consumption with brake horsepower.

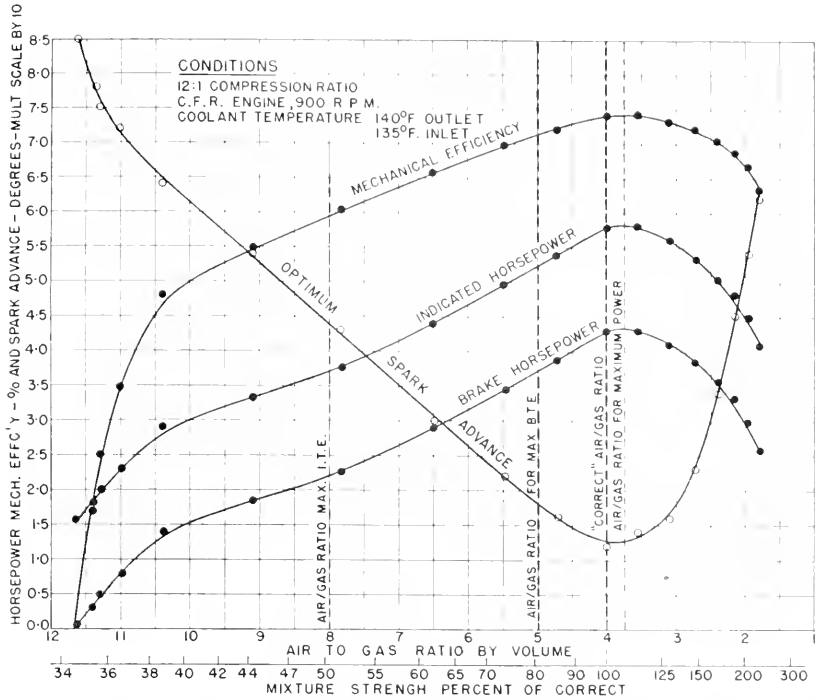


FIG. 2. Engine trial, jacket coolant 140° F. showing variation of power, optimum spark advance and mechanical efficiency with air-to-gas ratio and mixture strength.

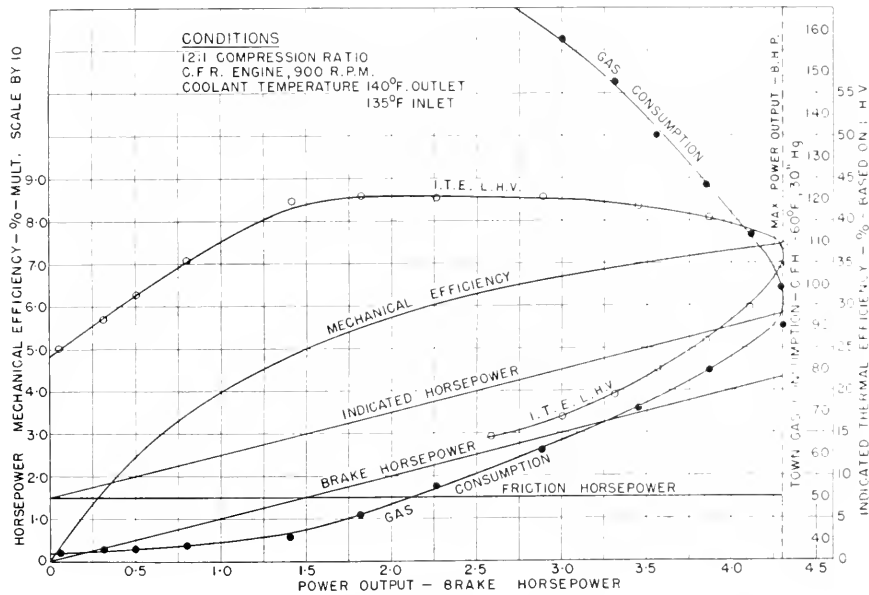


FIG. 2A. Engine trial, jacket coolant 140° F. showing variation of indicated thermal efficiency, mechanical efficiency and gas consumption with brake horsepower.

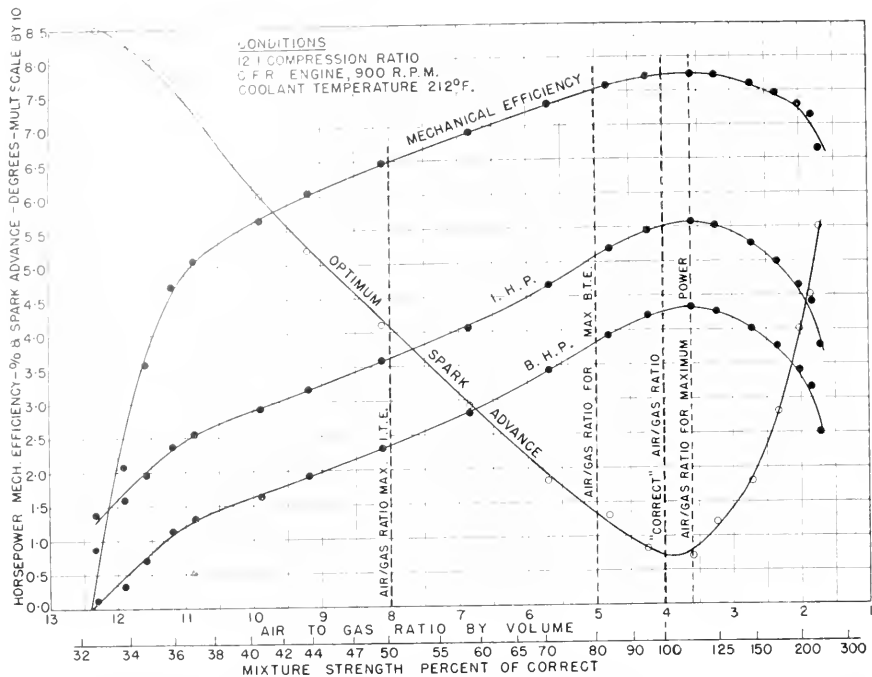


FIG. 3. Engine trial, jacket coolant 212° F. showing variation of power, optimum spark advance and mechanical efficiency with air-to-gas ratio and mixture strength.

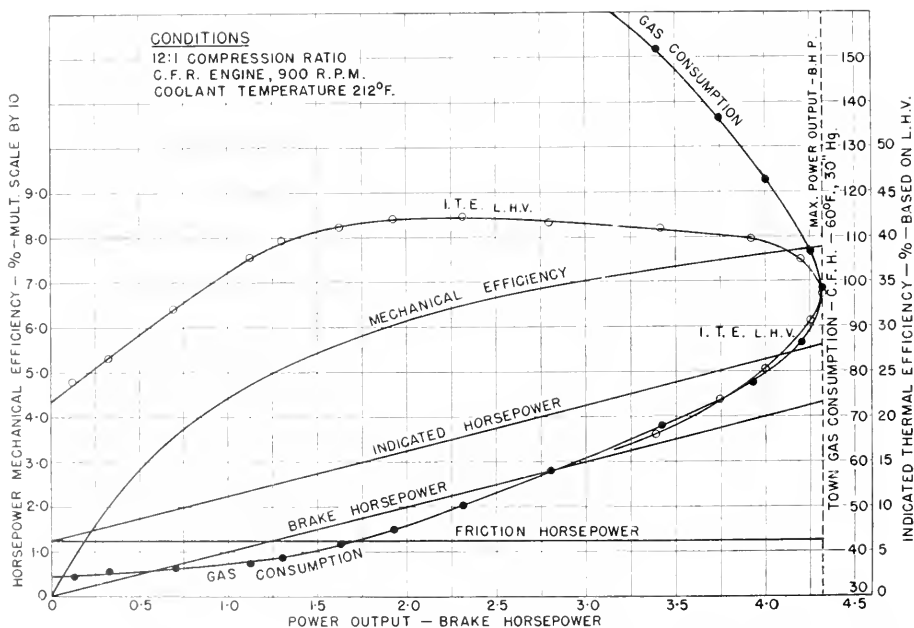


FIG. 3A. Engine trial, jacket coolant 212° F. showing variation of indicated thermal efficiency, mechanical efficiency, and gas consumption with brake horsepower.

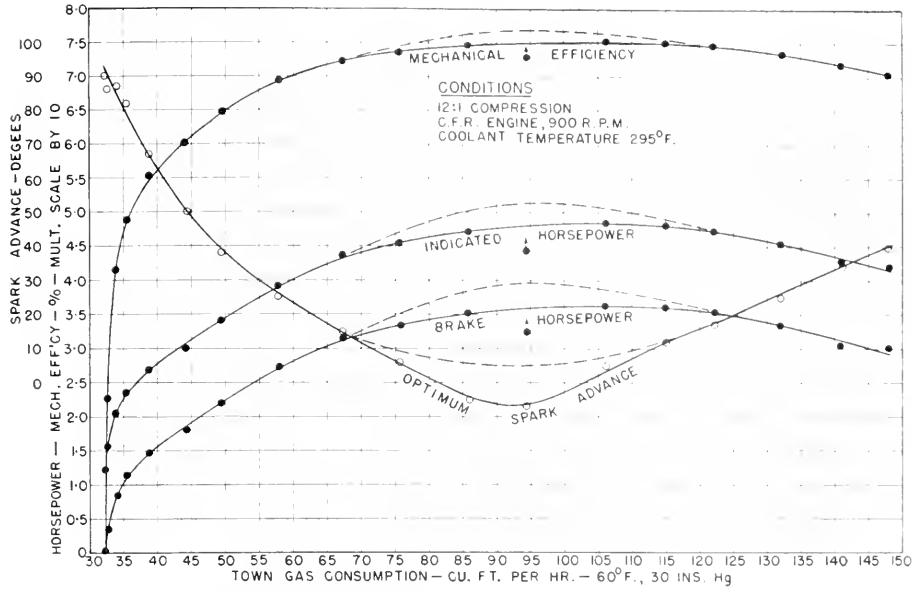


FIG. 4. Engine trial, jacket coolant 295° F, showing variation of power, optimum spark advance and mechanical efficiency with rate of gas consumption.

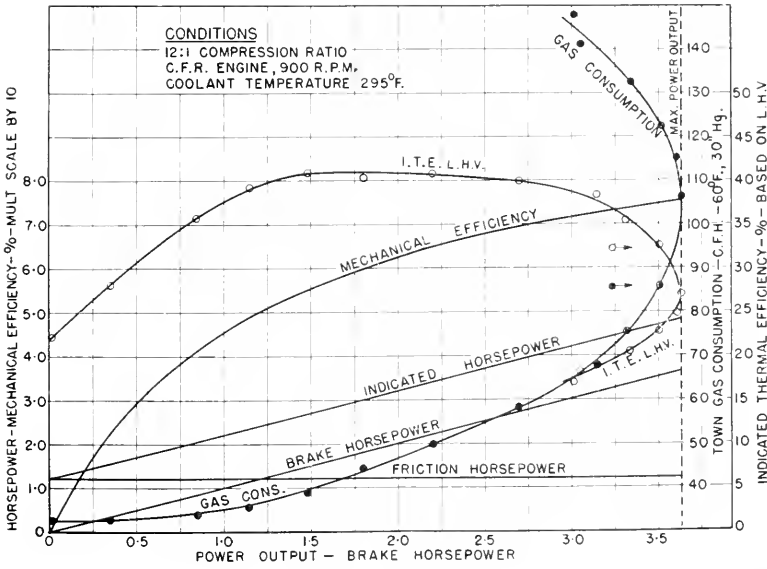


FIG. 4A. Engine trial, jacket coolant 295° F, showing variation of indicated thermal efficiency, mechanical efficiency, and gas consumption with brake horsepower.

MEASUREMENT OF POWER AND EFFICIENCY

A direct connected swinging field electric dynamometer provided with a beam type scale for weighing torque was used for the measurement of brake horsepower. Indicated horsepower was taken as the developed brake horsepower plus the brake horsepower required to drive the engine at the speed of the trials, immediately on ceasing to supply fuel. Thermal efficiency was calculated on the basis of the lower calorific value of the fuel gas as determined when trials were in progress.

EXPERIMENTAL RESULTS

The results of comprehensive trials made with jacket temperatures of 100° F., 140° F., 212° F., and 295° F. are given by a series of pairs of graphs. Thus the graphs of Fig. 1 for the trial at 100° F. jacket coolant give observed brake horsepower, indicated horsepower, optimum spark advance, and mechanical efficiency plotted on a base of air-to-fuel ratio by volume and the corresponding mixture strengths given as percentages of the "correct" value. The graphs of the companion figure, 1A, give collected results including indicated thermal efficiency, plotted on a base of brake horsepower.

The trial results obtained with jacket coolant temperatures of 140° F. and 212° F. are given by similar pairs of graphs, Figs. 2 and 2A and Figs. 3 and 3A.

The trial results obtained with a jacket coolant temperature of 295° F. indicated that performance was being limited by the incidence of preignition when mixture strength was increased to obtain greater than about 50% of maximum power. The combustion knock was not sufficiently serious to prevent observations being taken. They are plotted on a base of rate of gas consumption, Fig. 4, and on a base of brake horsepower, Fig. 4A; rate of air supply not having been measured. The broken lines, Fig. 4, indicate values that might have been obtained without preignition.

Significant data from the experimental results of all of the trials made at a compression ratio of 12 : 1 are given below in tabular form.

TABLE I
MAXIMUM INDICATED THERMAL EFFICIENCY (I.T.E.)
Data for variation with jacket coolant temperature

Coolant temperature, ° F.	100	140	212	295
Maximum I.T.E.	43	43	42	41
I.M.E.P., lb./sq. in.	90	87	85	80
Air-gas ratio by volumes	8	8	8	—
Mixture per cent weak	50	50	50	50

TABLE II
MAXIMUM INDICATED POWER (I.M.E.P.)
Data for variation with jacket coolant temperature

Coolant temperature, ° F.	100	140	212	295
Maximum I.M.E.P., lb. sq. in.	141	137	132	115
Corresponding I.T.E., %	36	36	31	27
Air-gas ratio by volume	3.75	3.75	3.6	—
Mixture per cent rich	10.7	10.7	11.1	—
Atmos. temp., ° F.	73.5	78.5	66.5	78.0
Atmos. press., in. Hg.	29.87	29.12	29.7	29.65

TABLE III
SEVENTY-FIVE PER CENT MAXIMUM INDICATED POWER
Data for variation with jacket coolant temperature

Coolant temperature, ° F.	100	140	212	295
75% of max. I.M.E.P.	108	103	99	86
Corresponding I.T.E., %	42.7	42.7	41.7	40.5
Air-gas ratio by volume	6.5	6.5	6.6	—
Mixture per cent weak	38	38	39	—
Atmospheric temperature and pressure as in Table II				

Discussion

The experiments were concerned with three principal features, namely, (1) performance in respect of power and thermal efficiency, (2) effect of mixture strength on thermal efficiency and the attainable degree of quality control, (3) performance of the spark ignition Otto cycle engine relative to that of the compression ignition Diesel type. The experimental results will be discussed in separate sections accordingly.

(1) *Performance at 12 : 1 Compression Ratio, as Limited by Surface Ignition with High Jacket Temperature*

The experiments with gaseous fuel were begun with hydrogen, Part V (6). It was found that the lubricating oil reacted with the hydrogen-air mixture to yield finely divided carbon having the appearance of lamp black. Knocking combustion and induction ignition occurred if the carbon were allowed to accumulate in the combustion chamber but not if it were brushed and blown out before beginning a trial.

The cleaning routine adopted accordingly was continued when town gas was used for the trials of Parts VI (7) and XII (5) and for those of this Part but did not yield any significant amount of finely divided carbon. The carbon derived from the lubricating oil appeared instead as a graphitic type which adhered firmly to surfaces in the combustion chamber, even those of the piston and exhaust valve. There was, in the circumstances, an absence

combustion due to nuclear ignition even at the very high compression ratio of 12 : 1. The knocking combustion that was obtained when jacket coolant temperature was raised to 295° F. indicated ignition by overheated surfaces. Thus, when maximum power was approached either from the weak or rich mixture side, the engine would run without spark knock but at reduced power and efficiency. The maximum power fell from 132 to 115 lb. per sq. in. I.M.E.P. on raising the jacket temperature from 212° to 295° F. and the related I.T.E. from 34 to 27%; see Table II and the graphs of Fig. 4 and compare graphs of Figs. 3A and 4A. It is indicated accordingly that Toronto town gas can be used at higher compression ratios than 12 : 1 if precautions are taken to avoid ignition of the gas by overheated surfaces.

The maximum power developed at 12 : 1 compression ratio cannot be compared on an equitable basis with that developed during the trials at 10 : 1, Part XII (5), because they were conducted without the restriction to the air supply introduced by using the throttle plate method of measurement. Moreover, when fitting the air flow measuring equipment for the trials at 12 : 1 compression ratio, it was a convenience to discard the inlet pipe to the carburetor. The consequence was the loss of the "ramming effect" noted in Part V (6, p. 271) as giving a power increase. Thus at 140° F. jacket temperature the maximum I.M.E.P. was 140 lb. per sq. in. at 10 : 1 C.R., Part XII, Table II, (5, p. 444), whereas it was lower at 137 lb. per sq. in. at 12 : 1 C.R., Table II *ante*. However, the jacket coolant temperature taken during the trials at 10 : 1 C.R. was that of the water outlet from the cylinder head but the *effective* coolant temperature might well be taken as the mean of the outlet temperature of 140° F. and the inlet temperature of 60° F., that is, 100° F. The I.M.E.P. of 140 lb. per sq. in. observed at 10 : 1 C.R. and coolant outlet temperature of 140° should therefore be compared with that obtained at 12 : 1 C.R. and jacket coolant at 100° F., which is also 140 lb. per sq. in., Table II *ante*. So the increase of power to be expected by raising the compression ratio from 10 to 12 : 1 was just offset by the restriction due to the use of a throttle plate for air flow measurement and the absence of a ramming effect.

The correction made as above does not seem to have given sufficient weight to the effect of the cold water inlet to the cylinder jacket to increase volumetric efficiency and power. Thus when evaporative cooling was used at both compression ratios, to provide 212° F. coolant temperature, maximum I.M.E.P., Table II *ante*, was 132 lb. per sq. in. at 12 : 1 C.R. and 125 lb. at 10 : 1, Table II, Part XII (5, p. 444); an increase of 5.6% on raising the compression ratio from 10 to 12 : 1.

The decrease of indicated thermal efficiency with increase of jacket coolant temperature for trials at 12 : 1 C.R. was similar to that described and discussed in Part XII, and further comment is not necessary.

(2) *Quality Control and the Decrease of Thermal Efficiency from a Maximum Value as Mixture Strength Diminishes*

It is generally supposed that thermal efficiency increases continuously as mixture strength diminishes and tends to approach the air standard value of $1 - \left(\frac{1}{r}\right)^{\gamma-1}$ where r is the compression or expansion ratio and γ the ratio of the specific heats of air. The above expression for efficiency is not concerned with the properties of the working fluid necessarily used in practice. It has been modified by Hopkinson (3) and by Tizard and Pye (13) to take into account increase of specific heat and dissociation with increase of temperature in an endeavor to obtain an expression for the ideal efficiency which can be more nearly approached, though not equalled, by a "real" engine. The proposed modifications leave the form of the expression for efficiency unaltered, therefore thermal efficiency at any particular expansion or compression ratio should approach the air standard value as the concentration of fuels in the mixture with air diminishes and the ratio of the specific heats of the working fluid approaches that of air only. Tizard and Pye (13, p. 12) conclude accordingly that "the indicated thermal efficiencies of the best engines are not likely to be improved upon substantially by any development of design other than that of the employment of weaker mixtures than can now be used," that is, aside from increasing the compression ratio.

The engine experiments using town gas at 10 : 1 C.R. described in Parts VI (7) and XII (5) gave some indication that thermal efficiency would not increase continuously as mixture strength was decreased but, after attaining a maximum, would decrease on further weakening of the mixture. The experiments could not be continued into the weak mixture region because of the failure of the ignition system at the high compression pressure corresponding to 10 : 1 C.R. even when the spark gap was reduced to 0.012 in., that is, to half the normal width of 0.025 in.

After the ignition system was improved as described in Section (a) of the Appendix, the spark gap was increased to 0.020 in., and it will be seen by reference to Figs. 1 to 4 and 1A to 4A that it was then possible to run the engine at 12 : 1 C.R. on mixtures so weak that brake horsepower was reduced to zero, 100% quality control with no throttle being attained accordingly.

Zero brake horsepower could not be maintained unless the controlling factors were kept nearly constant, as would be expected considering that the application of a slight load would cause a decrease of speed and that the corresponding decrease of power would prevent continued running.

The graphs of Figs. 1A to 4A show the rapid decrease of indicated thermal efficiency, from the maximum value, as zero brake horsepower is approached. Relevant data from the graphs are given below in tabular form.

TABLE IV
INCREASE OF INDICATED THERMAL EFFICIENCY WITH DECREASE
OF MIXTURE STRENGTH

Jacket coolant temp., ° F.	100	140	212	295
Maximum I.T.E., %	43	43	42	41
Corresponding air-gas ratio	8	8	8	—
Minimum I.T.E., %	27	25	23	22
Corresponding air-gas ratio	11.3	11.6	12.2	—

The air gas ratio of 8 required for maximum I.T.E. represents a mixture 50% weak. The air-gas ratio of 11.3, used when zero B.H.P. was developed at 100° F. jacket coolant temperature represents a mixture 65% weak. The extreme degree of weakness will be appreciated by remembering that the limiting value even for Diesel engines is regarded by Tizard and Pye as 50% (13, p. 12).

There are, so far as known, no previously published experimental results showing that thermal efficiency after attaining a maximum value decreases with decrease of mixture when town gas and other gaseous fuels, except hydrogen, are used for an Otto cycle spark ignition engine and that 100% quality control is possible. It might be thought that the novel results were obtained because of the extremely high compression ratio of 12 : 1 coupled with the somewhat special ignition arrangements. A compression ratio of 5 : 1 is commonly used for engines intended for running on town gas, and a trial was run accordingly and with the standard ignition system of the C.F.R. engine. The trial results are given by the graphs of Fig. 5, and it

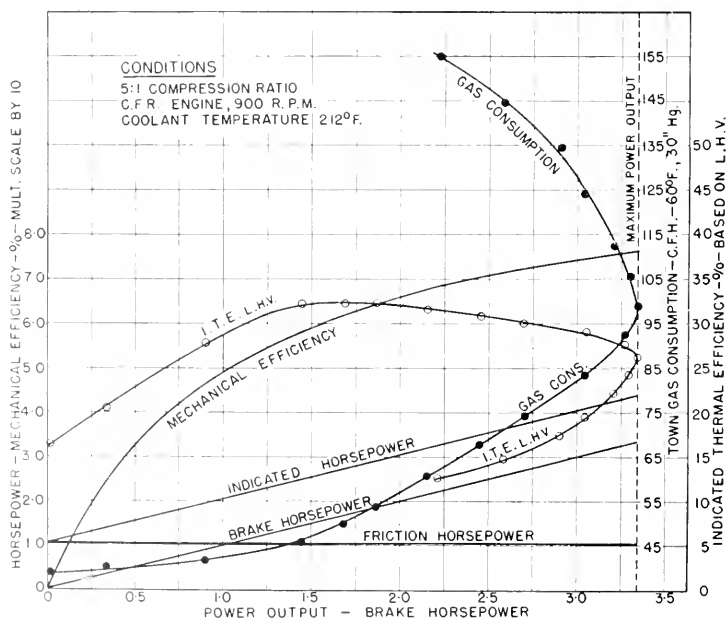


FIG. 5. Engine trial at 5 : 1 compression ratio showing variation of indicated thermal efficiency, mechanical efficiency, and gas consumption with brake horsepower.

will be noted that they follow the pattern of those obtained at 12 : 1 C.R., Figs. 1A to 4A. Indicated thermal efficiency after reaching a maximum value of 32.5% at approximately half load diminished to nearly 17% at zero brake horsepower. The percentage decrease was 48 as compared with 45% obtained at 12 : 1 C.R. when using the same jacket coolant temperature of 212° F. It is demonstrated, therefore, that the novel results in respect of quality control and thermal efficiency are not dependent on the use of extremely high compression ratios or on the use of special ignition arrangements.

It is of interest to compare the performance of the C.F.R. engine when using town gas at 5 : 1 compression ratio with that obtained by others at the same compression ratio when using a similar fuel in a different engine. The comprehensive trials made some years ago in the Engineering Laboratory of Cambridge University by A. F. Burstall and supervised by D. R. Pye are suitable for comparison purposes, having been described in the Transactions of the Institution of Automobile Engineers (London) (1) and the experimental results used liberally in text books by Pye and others.

The Ricardo E 35 variable compression engine (9), bore 4½ in., stroke 8 in., was used for Burstall's experiments. The C.F.R. engine, bore 3¼ in., stroke 4½ in., may be regarded as a small scale replica. Both engines have overhead valves and compression ratio is varied by mechanical movement of the cylinder head and barrel which is limited in the E 35 engine to afford a maximum compression ratio of 8 : 1. The similar mechanical arrangements of the C.F.R. engine permit a compression ratio of nearly 20 : 1 although the usual measurement arrangements provide for a maximum ratio of 10 : 1 only. The volumetric efficiency of the E 35 is relatively high because of the use of two inlet and three exhaust valves whereas the C.F.R. engine has but one of each. The E 35 engine has also the higher mechanical efficiency due mainly to the reduction of friction loss by the use of a short slipper type piston.

Burstall's trials with Cambridge town gas were run at engine speeds of 1000 and 1400 r.p.m. and over what was stated to be a wide range of mixture strength. Indicated thermal efficiencies determined at 1400 r.p.m. are shown by Pye (8, p. 178, Fig. 51) plotted against energy content per cubic foot of gas-air mixture. The figure includes graphs for the air standard efficiency and for the "theoretical" or ideal efficiency allowing for dissociation and increase of specific heat of the working fluid with increase of temperature. The figure is reproduced as Fig. 6, this Part, except that Burstall's results for 1000 r.p.m. are used as being the more nearly comparable with the results obtained for the C.F.R. engine at 900 r.p.m. Also, efficiencies, Fig. 6, are plotted against indicated mean effective pressures as being the more informative method for present purposes in that a thermal efficiency "loop" is obtained when the mixture strength is greater than required for maximum power.

It will be seen by reference to Fig. 6 that I.M.E.P. in Burstall's experiments, graph C, was reduced by reducing mixture strength to not less than the

value required for optimum thermal efficiency. I.M.E.P. was then 68 lb. per sq. in. and the line could be drawn through the somewhat scattered experimental points to be approximately parallel to graph *B* for ideal efficiency as given by Pye, no decrease of thermal efficiency with further decrease of mixture strength and I.M.E.P. being shown. Mixture strength in the C.F.R. engine experiment, graph *D*, was reduced until I.M.E.P. reached the lower value of 25 lb. per sq. in. and thermal efficiency diminished continuously in the circumstances from the maximum of 32.5% to 16.5%. Graph *D* is linear over the very weak mixture region and if extended would pass through the origin to show that when no gas is added to the air, and consequently no power developed, thermal efficiency would become zero instead of 47% as would be expected if thermal efficiency varied in accordance with the air standard, graph *A*, or the Tizard and Pye ideal standard, graph *B*.

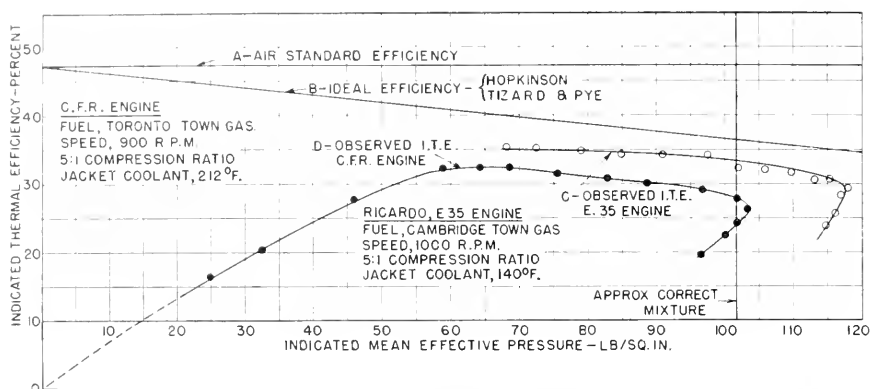


FIG. 6. Comparison of indicated thermal efficiency as obtained using C.F.R. and E 35 engines at 5:1 compression ratio, with "ideal" and air standard efficiencies.

The very great spark advance required for optimum ignition timing at very weak mixtures may afford a partial explanation for the decrease of thermal efficiency with decrease of mixture strength. A similar decrease has, however, been obtained with Toronto town gas when using an engine developing zero brake horsepower with a spark advance half as great as that required for the C.F.R. engine; moreover, special ignition arrangements were not required although the compression ratio was 9:1. Ricardo (10, p. 336) describes experiments with the E 35 engine for which zero brake horsepower was obtained when *hydrogen alone* was used as the fuel. The compression ratio was 5.15:1 and indicated thermal efficiency diminished from a maximum of 37% to 22% as mixture strength was reduced. Ricardo suggested that the decrease of thermal efficiency was "due to incomplete or retarded burning". Such effects would not be expected in view of the rapidity of hydrogen combustion and Ricardo mentions that "no misfiring or popping back into the carburetor occurred, the running being perfectly regular".

Graphs *C* and *D* of Fig. 6 show maximum indicated thermal efficiency to be higher for Burstall's experiments with the E 35 engine than for those with

the C.F.R. engine. The E 35 engine would be expected to yield the higher thermal efficiency because of the more favorable surface-to-volume ratio of the combustion space due to the relatively long stroke. Other factors require consideration. The higher speed used by Burstall accounts for a small part of the difference (8, p. 206). Valve timing might also afford a partial explanation except that in the E 35 engine it is reputed to be set for the higher speed of 1500 r.p.m. Another factor may be Burstall's method of calculating thermal efficiency. Thus it is stated (1, p. 617) that the higher calorific value of Cambridge town gas varied from 170 to 500 B.t.u. per cu. ft. and that an *average* lower value of 465 B.t.u. per cu. ft. was used in calculations. The possible error in the stated values of efficiency would then be $\pm 3\%$. A satisfactory feature of the comparison is that the thermal efficiencies given for the C.F.R. engine do not appear to have been overestimated.

(3) *The 12 : 1 Compression Ratio Performance of the C.F.R. Spark Ignition Engine Compared with that of Diesel Engines*

Comparison with Ruston Diesel Engine

The compression ratio of the Ruston engine in the heat engine laboratory, University of Toronto, is 14.4 : 1. Injection timing is fixed at 16° advance. The results of a staff trial made when the engine was in new condition are

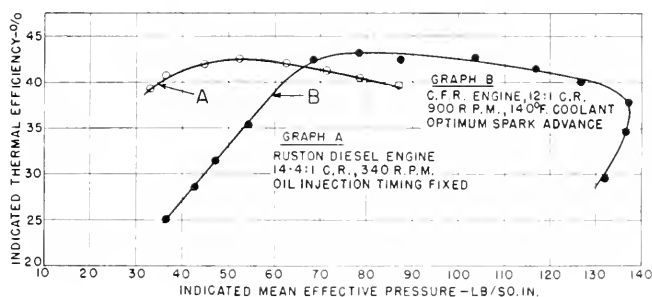


FIG. 7. Comparison of performance of C.F.R. engine with that of Ruston Diesel.

given by graph A of Fig. 7. The hydrocarbon oil used as fuel had a higher calorific value of 19500 B.t.u. per lb. Indicated thermal efficiency is calculated on the basis of the lower calorific value of 18280 B.t.u. per lb. The engine was run at the normal speed of 340 r.p.m.

The performance of the C.F.R. engine running at 900 r.p.m. and 12 : 1 compression ratio is shown by graph B, reproduced from Fig. 2A, *ante*.

A comparison of graphs A and B shows that the indicated thermal efficiency of the C.F.R. engine at 12 : 1 C.R. was slightly higher, at 43%, than that of the Ruston Diesel at 14.4 : 1. The maximum I.M.E.P. developed by the C.F.R. engine was 138 lb. per sq. in. as compared with 88 for the Ruston.

Comparison with Taylor Diesel engine

Taylor's experimental results (12, pp. 46-47) and those for the C.F.R. spark ignition engine were obtained at the same compression ratio, 12 : 1.

These results show that the best performance was obtained at 1000 r.p.m. as is shown by graphs *B* and *C* of Fig. 8. It will be seen that with correct injection timing, graph *C*, the thermal efficiencies of both engines were identical over the range of I.M.E.P. covered by Taylor's experiments. On the other hand, if injection timing were advanced as fuel supply was reduced, the Diesel engine efficiency became higher than that of the C.F.R. except in the region of maximum power where the two engines gave the same thermal efficiency; compare graphs *B* and *A*.

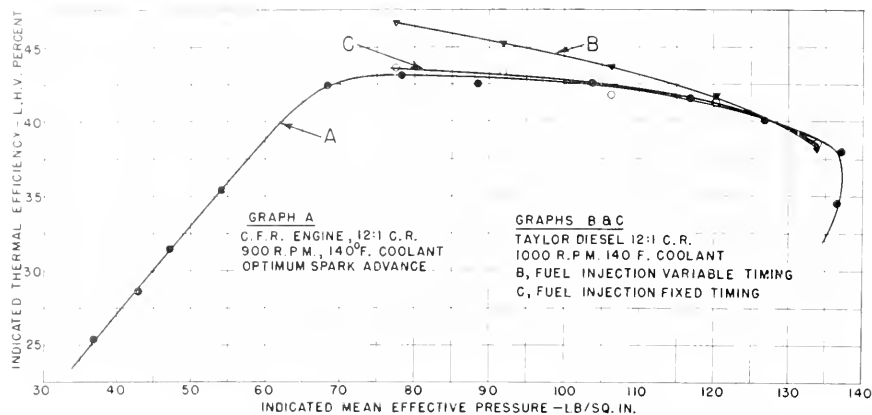


FIG. 8. Comparison of performance of C.F.R. engine at 900 r.p.m. with that of Taylor Diesel at 1000 r.p.m.

A comparison of performances when the speed of the Diesel was raised to 1200 r.p.m. is given by the graphs of Fig. 9. The thermal efficiency of the Diesel when injection timing is fixed is then well below that of the C.F.R. engine over the I.M.E.P. range of the Diesel; compare graphs *A* and *C*. When the Diesel injection timing was advanced as fuel supply was dimin-

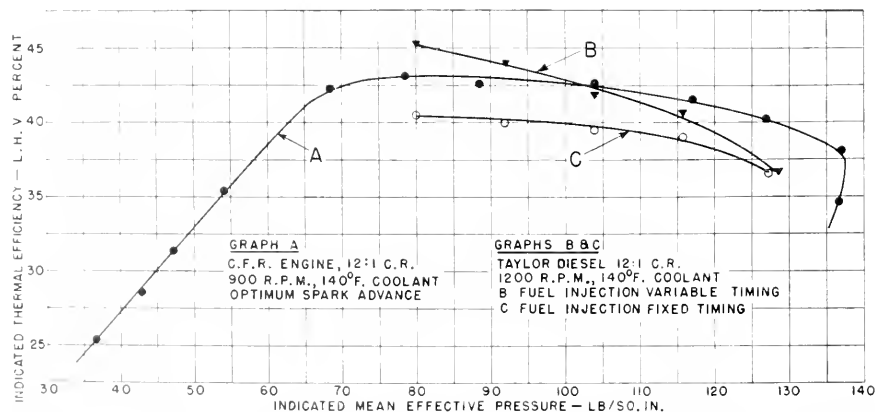


FIG. 9. Comparison of performance of C.F.R. engine at 900 r.p.m. with that of Taylor Diesel at 1200 r.p.m.

ished, thermal efficiency, graph *B*, rose to become higher than that of C.F.R. but over the lower part of the I.M.E.P. range only.

The ignition delay period is the besetting evil of the compression ignition type of Diesel engine and grows with increase of speed, resulting in a decrease of thermal efficiency and of range of useful load. The effects are shown by the graphs of Figs. 8 and 9. Thus at 1000 r.p.m. the range of I.M.E.P. is from 78 to 134 lb. per sq. in. but the small increase of speed to 1200 r.p.m. reduces the I.M.E.P. range to from 80 to 128 lb. per sq. in. The greater part of the reduction is at the higher end of the I.M.E.P. range, which for most purposes is the more useful end.

The delay period evil is not present in the spark ignition type of engine. Spark advance must be increased as mixture strength diminishes if optimum performance is to be maintained but the degree of advance depends mainly on turbulence, for a particular fuel. Turbulence increases with speed, and optimum spark advance tends to remain unchanged unless mixture strength is changed. It is for this reason that spark ignition engines are commonly run at speeds of 4000 to 5000 r.p.m., in special cases at 10,000 r.p.m. and higher. It will be of interest, therefore, to determine the effect of speeds higher than 900 r.p.m. on the performance of the spark ignition gas engine at 12 : 1 compression ratio.

Performance at 12 : 1 Compression Ratio Compared with that at 5 : 1

Experimental results given in this Part show the extent of the advantages to be gained in respect of power and efficiency by raising the compression ratio from the 5 : 1 commonly used for town gas to the unusually high value of 12 : 1. Significant data are given below in tabular form. Indicated thermal efficiency is stated as "efficiency" and values given for power (I.M.E.P.) are in pounds per square inch.

The trial at 12 : 1 C.R., unlike that at 5 : 1, was made with the air inlet slightly restricted for air supply measurement and without the ramming

TABLE V
DATA FROM TRIALS AT COMPRESSION RATIOS OF 5 AND 12 : 1
C.F.R. engine. 900 r.p.m. Jacket coolant, 212° F.
Horsepower $\times 23.6$ = Mean effective pressure, lb./sq. in.

Fuel, Toronto town gas	5 : 1 C.R.	12 : 1 C.R.	Observed ϵ_c increase	Corrected ϵ_c increase
Maximum efficiency, ϵ_o	32.3	42.2	30.6	
Corresponding I.M.E.P.	64.2	84.2	31.2	34.1
ϵ_c Efficiency at $\frac{3}{4}$ power	31.4	41.6	32.5	
Corresponding I.M.E.P.	77.6	99.0	27.6	30.5
ϵ_c Efficiency at max. power	26.2	33.7	28.6	
Corresponding I.M.E.P.	103.5	131.8	27.3	30.2

effect of the standard pipe inlet to the carburetor. The consequent loss of I.M.E.P. at maximum power was shown earlier to be at least 3.0 lb. per sq. in. or 2.3% of the measured value. A similar percentage increase should be applied to the I.M.E.P. observed at lower powers. Percentage increases of I.M.E.P. due to raising the compression ratio to 12 : 1, corrected accordingly, are given in the last column of Table V.

Acknowledgments

The experimental work was carried out with the co-operation of Prof. E. A. Mcutt, Head of the Department of Mechanical Engineering, University of Toronto, and Assistant Prof. W. A. Wallace. The cost was defrayed in part by an extra mural grant from the Defence Research Board of Canada. Mr. J. Alex. Morrison, supervisor of the appliance laboratory of the Consumers' Gas Company, Toronto, assisted by supplying necessary data in respect of the town gas used for the trials and newly calibrated special gas meters. Messrs. Holvarth and Powers of Sarco Canada, Limited, assisted with the design of the low temperature cooling system.

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APPENDIX

Section (a). Spark Ignition System

Coil ignition is standard for the C.F.R. knock testing engine. The breaker points of the system are normally open and a charge builds up on a 4 μ f. condenser in the primary circuit of the coil. When the cam allows the points to close, the condenser discharge through the primary circuit induces a high secondary voltage and a consequent spark across the gap of the spark plug. The system failed at compression ratios of 10 : 1 and higher unless the width of the spark gap were reduced to 0.012 in. from the standard of 0.025 in. Even so, spark ignition failed when mixture strength was less than about 50% weak.

The conditions required for the spark ignition of very weak mixtures were described by Cipriani and Middleton (2) just when arrangements were being made for the engine trials at 12 : 1 compression ratio. The ignition system of the C.F.R. engine was therefore revised in accordance with suggestions made by the first mentioned. The spark was made to pass on *breaking* the primary circuit, a new cam being provided accordingly. Minimum sparking voltage was obtained by using negative spark plug polarity; that is, the spark was passed from the ground to the center electrode. The large 4.0 μ f. condenser in the primary circuit was not required but one of a tenth the capacity was placed across the breaker points to suppress pitting. A heavy duty 12 v. Auto-Lite coil was used and a one inch spark obtained at atmospheric pressure as compared with the one-quarter inch spark of the standard ignition system. The improved system was used for the engine trials at 12 : 1 compression ratio and, at full throttle, ignited gas-air mixtures so weak that 100% quality control was obtained.

Section (b). Automatic Method of Maintaining Jacket Water at Low Temperatures

The method comprises a pump maintained water circulation combined with automatic control of the temperature of the water admitted to the lower end of the jacket and control of the rate of flow to maintain a small difference of temperature between the inlet and outlet of the jacket.

The layout of the method is shown diagrammatically by Fig. 10. Cold tap water enters one side of the "Sarco" water blender (11) and hot water from the engine jacket, the other side. When the pressures of the hot and the cold water are equal the blender can be set to deliver a mixture at a pre-determined temperature. Equal pressures are obtained by the use of a pressure reducing valve on the cold tap water supply and a constant pressure

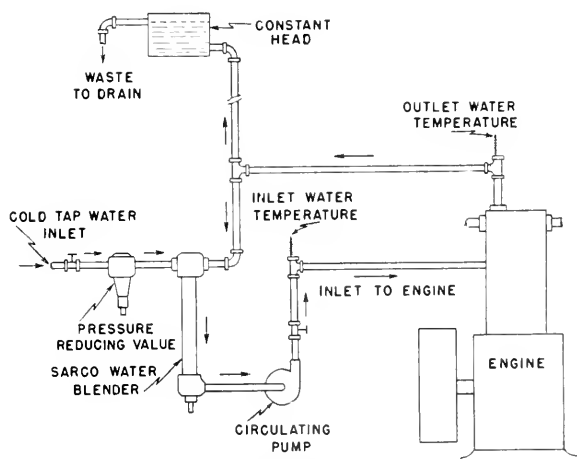


FIG. 10. Arrangement for automatic regulation of jacket water temperature

to 100 to 1000 water supply from the engine jacket. The blender then mixes water from the engine at the rate required to raise the temperature of the 1000 water supply to the predetermined value. Any surplus of hot water flows back to the constant head. The rate of delivery of constant temperature mixture, required to maintain the temperature rise in jacket of say from 5° to 6° F., is set by adjusting the opening of the valve on the discharge side of the circulating pump which is driven at constant speed by an electric motor.

Section (c). Air Supply Measurement

The air box orifice method of measuring the rate of air supply to an engine consists essentially of a receiver into which air passes through a metering orifice and from which it is drawn by the engine at an equal rate, in the absence of leakage. The rate of air flow into the receiver can be calculated from the observed difference of pressure across the orifice if the coefficient of discharge be known.

Coefficients for easily reproducible square edged orifices in thin plates were measured with an accuracy approaching 1/5 of 1% by Watson and Schofield (11) and in conditions especially applicable to the measurement of the air supply to an engine. Their measurements, unlike those of others, were made with air flowing *into* the receiver and for pressure differences across the orifices not greater than 2 in. of water in order to avoid any considerable throttling effect.

The sole difficulty in using the coefficients to measure the air supply to an engine arises from their having been determined for steady air flow whereas the flow into a piston engine is pulsating. Corrections were devised accordingly by Watson and Schofield but it is simpler to reduce pulsations to negligible proportions by using a receiver of sufficient capacity than to obtain the data necessary for the corrections. The capacity in cubic feet to be used is, according to King (4), given by the expression,—

$$600 \times \frac{\text{Hp. to be measured}}{\text{No. of cylinders} \times \text{r.p.m.}}$$

The capacity of the receiver required when measuring the air supply to the C.F.R. engine developing 3 hp. at 900 r.p.m. would therefore be 2.0 cu. ft. It is, however, stated by King that capacities less than 5 cu. ft. are not recommended and that a single cylinder engine must be treated as a special case.

The arrangements made accordingly for measuring the rate of air supply to the C.F.R. engine are illustrated by Fig. 11. Two receivers of approximately 8 cu. ft. each were connected in series. A clean, 45 imperial gallon oil drum of the usual type with dished ends was used as the first receiver. The second receiver was a drum of the type used for transporting charcoal. One end of that type is provided with a removable *flat* steel cover plate. The plate is shown in elevation by the diagram. It was provided with four

2½ in. diameter holes over which the thin orifice plates could be placed without distortion and sealed with plasticene. Orifices not in use were closed by means of soft rubber stoppers. The special arrangements shown by the diagram for passing the air from one receiver to the other and thence to the engine were devised to reduce air oscillation. The 2 in. gas pipes passing through the receivers were brazed in place and the lengths inside drilled with 1 in. holes straight through.

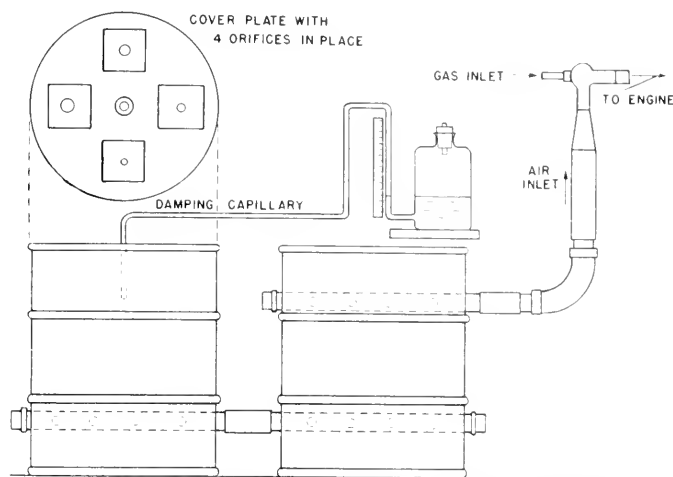


FIG. 11. Arrangement for metering air supply to engine.

The orifices were lathe bored in 4½ in. squares of tin plate 0.017 in. thick while clamped between heavy steel plates. Orifices made in this way have truly square edges nearly free of burr and can be used for accurate measurement of air flow by calculation based on the coefficients of discharge determined by Watson and Schofield. The coefficient varies slightly with orifice diameter and pressure difference; corrections from an average value of 0.60 must be made accordingly if an accuracy of better than 1.0% is desired. An orifice of 5.8 in. diameter was used for measurement of the air supply to the C.F.R. engine when run at 900 r.p.m.

A single leg manometer filled with low viscosity white paraffin oil was used for the measurement of pressure differences. The oil gives a better meniscus than water and a greater reading for the same pressure difference. An oscillation of about 3.0 mm. in the oil column was reduced to less than 1.0 mm. by the damping capillary shown by the diagram.

**THE OXIDATION, IGNITION, AND DETONATION OF FUEL
VAPORS AND GASES**

**XIV. THE CAUSE OF THE EFFECT OF HYDROGEN SULPHIDE TO REDUCE
THE COMPRESSION RATIOS AT WHICH FUEL GASES CAN BE USED
IN SPARK IGNITION ENGINES**

BY R. O. KING, E. J. DURAND, BERNARD D. WOOD,
AND A. B. ALLAN

THE OXIDATION, IGNITION, AND DETONATION OF FUEL VAPORS AND GASES

IV. THE CAUSE OF THE EFFECT OF HYDROGEN SULPHIDE TO REDUCE THE COMPRESSION RATIOS AT WHICH FUEL GASES CAN BE USED IN SPARK IGNITION ENGINES¹

By R. O. KING,² E. J. DURAND,³ BERNARD D. WOOD,⁴ AND A. B. ALLAN⁵

Abstract

Experimental results are given for trials of the C.F.R. engine at 900 r.p.m. and 12 : 1 C.R. on Toronto town gas alone and with an addition of hydrogen sulphide. The sulphide led to such severe preignition that measurements of power were impossible except for very weak or very rich mixtures. The former included the 50% weak mixture for which thermal efficiency is a maximum. The sulphide was then of beneficial effect, a maximum value of 44% for indicated thermal efficiency being obtained as compared to a maximum of 42.5% without it. The experimental results are interpreted in the light of combustion tube experiments showing that hydrogen in mixtures with air is not ignited by red hot surfaces on which it is oxidized with sufficient rapidity to steam, but that ignition occurs at relatively low temperatures if the surface reaction is inhibited by hydrogen sulphide. The conclusion is that fuel gases containing hydrogen in large proportion can be used for full power engine operation at compression ratios even higher than 12 : 1 if the oxidation of the hydrogen in part to steam, on the hot surfaces in the combustion chamber, is not inhibited by the poisoning effect of the hydrogen sulphide commonly present in the gases.

Introduction

The compression ratio of 12 : 1 at which Toronto town gas was used for the engine trials described in Part XIII (7) is impossibly high according to accepted standards. Ricardo, for example, states (15, p. 32) that the usable compression ratio for town gas is 5 to 6 : 1, for producer gas 6 to 7 : 1, for blast furnace gas 7 to 7½ : 1, and for coke oven gas which frequently contains over 50% of hydrogen the safe compression ratio is little if any greater than 5 : 1. Lucke is even more specific in respect of the role played by hydrogen. He states (12, p. 33), "gases rich in hydrogen generally preignite easily; approximately one atmosphere should be deducted from the compression allowable with no hydrogen for each 5 per cent of hydrogen present". The "safe" compression pressure given accordingly in Kent (4, 12-41) is 90 to 100 lb. per sq. in. gauge for coke oven gas which contains hydrogen in greater concentration than is found in other fuel gases. The views mentioned in respect of hydrogen appear to be confirmed by the experiments of Ricardo (16) and A. F. Burstall (2). Their experiments are discussed at some length

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by Pye (14, pp. 188-190) who after describing the operation of the E 35 engine on extremely weak hydrogen air mixtures concludes, "the same faculty of rapid flame propagation which makes burning possible on the weak side, makes it impossible to work at the rich end of the scale of fuel-air ratios even up as far as the correct mixture. Whenever running was attempted with a hydrogen-air ratio more than about 95 per cent of that giving complete combustion, violent preignition set in, accompanied by firing back through the carburetor. This happened even when the compression ratio was lowered to 3.8 : 1 while at higher ratios smooth running was limited to even weaker mixtures."

The experimental results for engine trials with hydrogen and town gas, described in Parts V (10), VI (11), XII (6) and XIII (7), are completely at variance with those presently accepted as a basis for the authoritative conclusions mentioned above. Hydrogen has been used at compression ratios extending to 10 : 1 at any mixture strength and without preignition (10); town gas containing hydrogen in a concentration nearly as great as in coke oven gas has been used similarly at a compression ratio of 12 : 1 (7), the compression pressure then being 390 lb. per sq. in. gauge as compared with the "safe" value of 80 to 100 lb. given in "Kent". Moreover, the performance in respect of power and thermal efficiency was commensurate with the unusually high values of the compression ratio which at 12 : 1 was just within the Diesel engine range. It is indicated accordingly, and is illustrated by the experiments of Part XIII (7), that the spark ignition Otto cycle engine may be made to surpass the Diesel in respect of both power and thermal efficiency. It is thermodynamically possible because both types now use the Otto cycle, and combustion characteristics are the better for the carburetor spark ignition type.

The great increase in power and thermal efficiency obtainable by using fuel gases at Diesel engine compression ratios would be of economic importance if it could be realized in practice. It may be considered, therefore, that the object of the investigation presently in hand is in part to discover why it has been necessary to operate the spark ignition gas engine at the relatively low compression ratios for which power and thermal efficiency are necessarily inferior. The experimental results described in earlier Parts provide a partial explanation only. The experiments of this Part were planned in the hope of completing the explanation.

It was shown by the experiments with hydrogen alone, Part V (10), that preignition accompanied by firing back through the carburetor was due to ignition of the hydrogen-air mixture by finely divided carbon derived from the decomposition and oxidation of the lubricating oil, but starting with a clean engine some hours running was required for the necessary accumulation of carbon. On the other hand, the decomposition and oxidation of the lubricating oil did not yield finely divided carbon to the same extent when Toronto town gas was used as engine fuel, as noted in Part XIII (7). It

seemed that the engine could run for an indefinite period without preignition if a normal jacket temperature were maintained. Such a result, according to experience in practice, would be an impossibility if coke oven gas were used although the proportion of hydrogen in it is not substantially greater than in Toronto town gas. The gases differ mainly in respect of sulphur concentration. Toronto town gas is nearly free of hydrogen sulphide and contains organic sulphur in the extremely small concentration of 10 to 15 grains per 100 cu. ft., as mentioned in Part XIII (7), whereas the concentration in coke oven gas may be as great as several hundred grains per 100 cu. ft. and may extend to several thousand in refinery gases from sulphur crudes and in natural gases from sulphur bearing regions (13, p. 2362).

It appears, therefore, that hydrogen sulphide is the chief sulphur impurity in fuel gases. It is known that the substance promotes preignition, and the experiments of this Part were made to determine the extent and cause of the effect.

Experimental Arrangements and Results

The experimental arrangements were as described in Part XIII (7) plus means for adding hydrogen sulphide at a measured rate to the air-gas mixture. The hydrogen sulphide was obtained from the Matheson Co. in a high pressure steel cylinder from which it was drawn as required through a special pressure regulator. It was supplied at atmospheric pressure at the rate of 4.8 cu. ft. per hr. to the air-gas mixture used by the engine. The rate was the minimum that could be measured accurately by the available dry gas meter and is approximately 5.0% by volume of the rate of town gas required for maximum power.

The hydrogen sulphide was taken to have the higher calorific value of 630 B.t.u. per cu. ft. at 60° F. and 30 in. of mercury as given in works of reference. The lower calorific value was then 581 B.t.u. per cu. ft. in the standard conditions of temperature and pressure and was used for calculations of thermal efficiency.

The engine trials were run at 12 : 1 compression ratio, an engine speed of 900 r.p.m. and with the jacket coolant at 212° F. Although data were available for a trial made earlier when using town gas in the conditions mentioned, there was some uncertainty about the condition of surfaces in the combustion space, the engine not having been dismantled for cleaning since the beginning, some three months earlier, of the trials with town gas described in Part XIII (7). It was planned, therefore, to run a new trial with town gas, after cleaning the combustion space by means of a brush and scraper inserted through the spark plug and bouncing pin holes; a great deal of surface area could not be reached in this way. The trial was then to be followed by one with the addition of hydrogen sulphide to the gas-air mixture.

The trial with town gas alone was begun on Sept. 8, 1949, but was discontinued because dust from concrete work in progress nearby the engine induced

knocking combustion. A similar proknock effect had been obtained from concrete dust a year earlier when hydrogen was being used as the fuel for the same engine (9).

The work was resumed the next day, the dust concentration in the laboratory atmosphere having become normal, and the two trials were completed during the period 7 a.m. to 11 p.m. Measurements were made of brake and indicated horsepower and of rates of air and gas supply. Optimum spark advance as determined by prior experiments was always used. The experimental results are given by the graphs of Figs. 1 to 3.

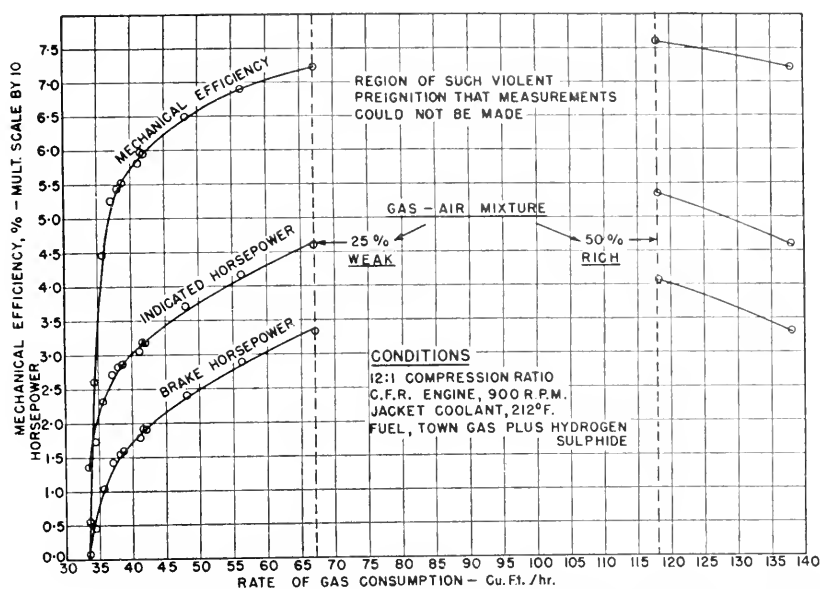


FIG. 1. Observed values of indicated horsepower and mechanical efficiency corresponding to rate of gas consumption.

Brake horsepower, indicated horsepower, and mechanical efficiency plotted on a base of rate of supply of town gas plus hydrogen sulphide are given by the graphs of Fig. 1. It will be noted that at rates of gas supply from 67 to 117 cu. ft. per hr. preignition was so violent that measurements of power could not be made, and it was unsafe to try to continue running the engine. Measurements were possible only at very weak or very rich gas-air mixtures as shown by the graphs.

Horsepower and mechanical efficiency measurements plotted on a base of air-to-gas ratio by volume and mixture strength percentages are shown by the graphs of Fig. 2. The value of the correct air-gas ratio shown on the figure as approximately 4.25 is the mean of values with and without hydrogen sulphide, which possesses a higher calorific value than the town gas. It will be noted that the mixture strength region over which operation of the engine

was prevented by preignition was from 25% weak to 50% rich. Preignition was pronounced even with the mixture 25% weak but was not sufficiently severe to prevent measurement.

It is not necessary to give in detail the results of the trial made when using town gas alone. They confirmed those obtained earlier in the same conditions which are shown by the graphs of Figs. 3 and 3, A, Part XIII (7), except

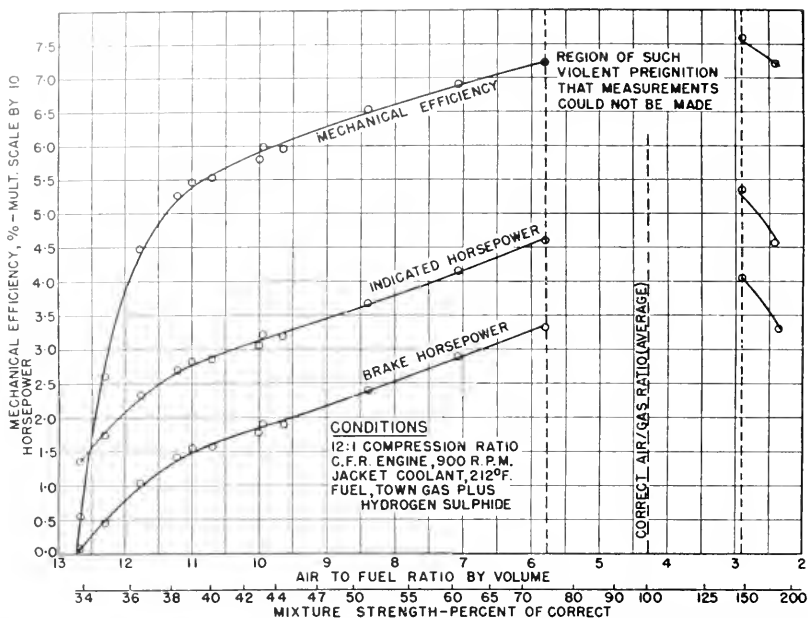


FIG. 2. Observed values of indicated horsepower and mechanical efficiency corresponding to air-to-gas ratio or percentage mixture strength.

that a slightly higher value of 43% was obtained for maximum indicated thermal efficiency as compared with the 42% of the earlier trial. The essential data for a comparison of the results of the two trials are given by the graphs of Fig. 3 for indicated thermal efficiencies plotted on a base of indicated mean effective pressure.

It will be seen by reference to the graphs that a maximum value of 44% was obtained for indicated thermal efficiency when the gas-air mixture contained hydrogen sulphide. This is an increase of 2.3% on the value obtained without hydrogen sulphide during the trial made earlier the same day and an increase of 4.8% on the value obtained for the trial described in Part XIII (7) when using a jacket coolant at 212° F. Maximum indicated thermal efficiency was obtained at about half power with a gas-air mixture 50% weak. On going to still weaker mixtures the value was progressively less affected by the hydrogen sulphide.

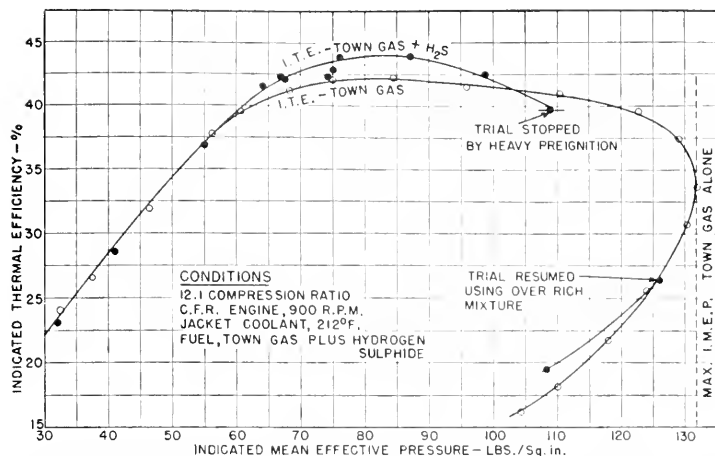


FIG. 3. Relation between indicated thermal efficiency and indicated mean effective pressure with and without hydrogen sulphide in gas-air mixture.

Preignition developed almost immediately on going to richer mixtures. Thermal efficiency diminished at a relatively high rate and preignition became so violent when values of the I.M.E.P. exceeded 109 lb. per sq. in. that measurements could not be made. The mixture strength was then increased to be 50% rich. Preignition did not occur and measurements could again be made.

The Residual Sulphur Effect

The experiments made with sulphur added to liquid fuels, described in Part III (5), disclosed the existence of a marked residual effect. It persisted even after the usual thorough cleaning of the combustion chamber surfaces with the engine dismantled and caused knocking combustion even when benzene was used at moderate compression ratios. The knocking combustion did not stop until after the engine had again been dismantled and the combustion chamber surfaces given a second and more drastic cleaning.

It was expected accordingly that a similar residual effect might exist after using town gas plus hydrogen sulphide even for the relatively short time of about five hours taken for the experiments described in this Part. The existence of the effect was verified by experiments. The engine was then dismantled and the combustion chamber surfaces drastically cleaned, special attention being given to the piston crown and the exhaust valve. Some residual effect was observed on again using the engine, and a period of 70 hr. running on a weak pentane-air mixture was required before the standard knock intensity corresponding to a particular octane-heptane mixture was regained.

Discussion

It was shown by experiments described in Part III (5, pp. 137-139) that a pentane-air mixture in combining proportions, passing through a red hot, 670° C., 1238° F., steel combustion tube would not ignite and explode because

of the sulphide of its inflammability by dilution with the steam and carbon dioxide, and the surface oxidation. If, however, hydrogen sulphide were added to the pentane-air mixture, ignition and explosion occurred at $580^{\circ}\text{C}.$, a temperature corresponding to less than a dull red heat. It is well known that in the circumstances the effect of the hydrogen sulphide is to convert the surface of the steel tube to iron sulphide which is inactive to oxidize hydrocarbons to steam and carbon dioxide or hydrogen to steam.

It was shown further by experiments described in the reference quoted that the surface effect to inhibit oxidation to steam and carbon dioxide remained when the hydrogen sulphide was no longer added to the pentane-air mixture, explosion then occurring at a temperature $10^{\circ}\text{C}.$ only higher than when the hydrogen sulphide was present in the mixture. The residual effect supports the view that neither the inhibitory action of hydrogen sulphide on the reaction to steam and carbon dioxide nor the reaction itself is other than a surface effect. Furthermore, it may be concluded that the degree of the inhibitory effect depends on time of exposure of the steel surface to the action of hydrogen sulphide as well as to the concentration of that "catalytic poison" in the combustible mixture.

The effect of steam formed by the oxidation of *hydrogen* in mixtures with air, on a surface of iron oxide to raise the ignition temperature, is shown by experiments also described in Part III (5, p. 128). Thus on passing the mixture through a silica tube, rate of oxidation of the hydrogen to steam was just measurable at $550^{\circ}\text{C}.$ and explosion occurred at $587^{\circ}\text{C}.$ When, however, the surface of the tube became partly coated with iron oxide, the hydrogen oxidized to steam with great rapidity and a temperature of $667^{\circ}\text{C}.$ was required for ignition.

It will be noted that the igniting temperature of $587^{\circ}\text{C}.$ for hydrogen in contact with an inactive silica surface is nearly the same as that of $590^{\circ}\text{C}.$ for a pentane-air mixture on a steel surface made inactive by the poisoning effect of hydrogen sulphide.

The effect of surface reactions occurring when town gas is used in an engine can now be described. The principal constituents of the gas are hydrogen, carbon monoxide, and methane, and in the Toronto variety the approximate percentage concentrations are 50, 22, and 12 respectively. The average igniting temperatures of the gases in mixtures with air, given by Coward (3) as having been determined by H. B. Dixon when using a combustion tube having an inactive, porcelain, surface are, hydrogen $585^{\circ}\text{C}.$, carbon monoxide $650^{\circ}\text{C}.$, and methane $700^{\circ}\text{C}.$ Therefore hydrogen, having the lowest surface ignition temperature and forming by far the largest constituent of town gas, would be expected to be responsible for preignition when it occurs in gas engines, a view in accordance with statements made in textbooks. The view is correct solely if the surfaces in the combustion space are *inactive* to oxidize the hydrogen to steam. *Active* surfaces can be raised to temperatures

higher than a red heat without igniting hydrogen-air mixtures in contact with them as illustrated by the graphs of Fig. 4. The graphs give the igniting temperatures for hydrogen-air mixtures passing through silica and stainless steel combustion tubes and are selected from experimental results obtained by King and Mole (8). Ignition occurred in the silica tube at a temperature as low as 565°C . It was not greatly affected by the concentration of hydrogen in the mixture which in the conditions was inflammable for contractions varying from 5 to 90%. The minimum igniting temperature of the mixture in contact with the steel surface was 630° and mixtures containing hydrogen in concentrations less than 20% or greater than 30% could not be ignited even at the measurable maximum of 750°C .

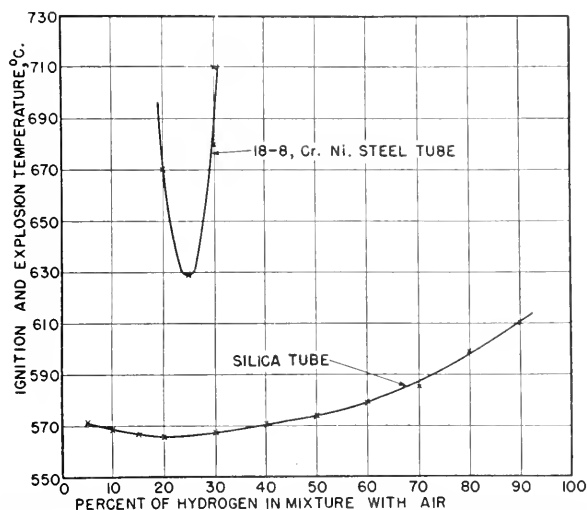


FIG. 4. Igniting temperatures and range of inflammability of hydrogen-air mixtures passing through open combustion tubes 1 in. internal diameter. Mixtures supplied at the rate of 150 cc. per min.

The conclusion is that the hydrogen constituent of a fuel gas is of useful effect to prevent preignition but of evil effect if the combustion chamber surfaces are such that oxidation thereon of the gas to steam cannot occur. Initially clean steel or iron surfaces in the combustion space become coated with metallic oxide almost immediately on running the engine under power. Steam is formed on the reduction of the oxide by the hydrogen, and compression ratio can be raised to values even higher than the 12:1 used for the trials of this Part, without the occurrence of preignition or detonation. The steam not only prevents preignition by hot surfaces but by reducing the inflammability of the end gas counteracts the igniting effect of finely divided carbon derived from pyrolysis of the lubricating oil to promote detonation. The steam forming reaction is continuous because in equilibrium conditions the rate of reduction of the oxide by hydrogen is equal to the rate of oxide formation by the oxygen in the gas-air mixture. The evil effect of hydrogen

becomes apparent when the surface reaction to form steam is inhibited by hydrogen sulphide because the surface ignition temperature of hydrogen then becomes lower than that of the other gases present in appreciable proportion in town gas.

All of the above mentioned effects are exemplified by the experiments of this Part made with combustion chamber surface temperature rising from that corresponding to zero brake horsepower to that attained at maximum power and then decreasing as power decreases with the use of overrich mixtures. Refer now to Fig. 3, and follow the graphs beginning with the minimum I.M.E.P. of 30 lb. per sq. in. for which brake horsepower is zero. It will be seen that indicated thermal efficiency values remain the same with and without hydrogen sulphide in the gaseous mixture until I.M.E.P. exceeds 60 lb. per sq. in. That is, the heat developed over the low power range is insufficient to raise surface temperature to the degree required for the oxidation of hydrogen to steam at an appreciable rate. There is then no reaction to be inhibited by the hydrogen sulphide and it provides merely part of the heat value of the combustible mixture, taken into account in calculating thermal efficiency.

The graphs diverge at the surface temperature attained when power exceeds 60 lb. per sq. in. I.M.E.P., indicating that rate of surface oxidation of the hydrogen to steam has become appreciable because thermal efficiency rises when the reaction is inhibited by the poisoning effect of the hydrogen sulphide.

The maximum value of the thermal efficiency attained on inhibiting the steam forming reaction is 44% as compared with the average maximum of 42.5% obtained otherwise. The maximum values were however always obtained for mixtures 50% weak and at corresponding surface temperatures. On using richer mixtures to increase power and consequently surface temperature, preignition became noticeable for the mixtures containing hydrogen sulphide and so heavy when I.M.E.P. exceeded 109 lb. per sq. in. that it was necessary to stop the engine. It was possible, however, to resume the trial at the lower surface temperature corresponding to a mixture 50% rich and to obtain then a slight increase of indicated thermal efficiency with hydrogen sulphide in the gaseous mixture, presumably because then the beneficial effect of inhibiting steam formation can be realized without the incidence of preignition, just as occurred when weak mixtures were used.

Concluding Comment

The experiments of this Part and those of Parts XII (6) and XIII (7) demonstrate that the hydrogen content of fuel gas free of sulphur renders it possible to run a gas engine at Diesel engine compression ratios, but at the expense of some slight loss of possible thermal efficiency. Thus the maximum thermal efficiency obtained at 10:1 compression ratio, Part XII, was 41% which is 68.5% of the air standard value of 59.8%. The maximum value

(average) of the trials made at 12 : 1, Part XIII and this Part, was 42.5% which is 67.9% of the corresponding air standard value of 62.6%. When the gaseous mixture contained hydrogen sulphide and the steam forming surface reaction was inhibited, maximum thermal efficiency rose to 44% which is 70.3% of the air standard value.

Maximum thermal efficiency is however obtained for a gas-air mixture 50% weak. As the mixture is enriched to increase power and consequently surface temperature, the formation of steam by surface reaction becomes increasingly necessary for the prevention of preignition. Without the steam forming reaction, which is made possible by the hydrogen content of the fuel gas, the engine can be run at high compression ratios on light loads only.

The concentration of sulphur in fuel gas required to prevent the use of high compression ratios as mixture strength and power are increased from relatively low values has not been determined. The concentration of 10 to 15 grains of organic sulphur in Toronto town gas seemed to be without ill effect. The degree of concentration is probably of little importance because of the residual effect. Thus a small concentration, but exceeding a possible threshold value, used for a long period would be expected to have the same poisoning effect on the surface as a larger concentration used for a short one.

The experiments described in this Part have been solely those showing that it is the *combined* effect of hydrogen and hydrogen sulphide which limits the use of fuel gases containing hydrogen in large proportion to the compression ratios of from 5 to 5.6 : 1 currently used in practice. The *combination* is of evil effect also in respect of cylinder wear. Thus Broeze and Gravesteyn (1) conclude that, at the high temperatures and pressures attained in the combustion space of Diesel engines, sulphur trioxide, rather than the dioxide, is formed and that the sulphuric acid arising from reaction of the trioxide with steam can account for a high rate of cylinder wear.

A further sulphur effect not dealt with in this Part is the proknock action of certain of the compounds arising from nuclear ignition of the end gas on their decomposition to finely divided sulphur. It is to be noted also that the use of so high a compression ratio as 12 : 1 for town gas free of sulphur is possible if the air supply does not contain an unusual concentration of dust and if the lubricating oil does not decompose to yield sufficient finely divided carbon for nuclear ignition.

Acknowledgments

The experimental work was carried out with the co-operation of Prof. E. A. Allcut, Head of the Department of Mechanical Engineering, University of Toronto, and Assistant Prof. W. A. Wallace. Mr. J. Alex. Morrison, supervisor of the appliance laboratory of the Consumers' Gas Company, Toronto, assisted by supplying necessary data in respect of the town gas used for the trials and newly calibrated special gas meters. Mr. S. Sandler

The Defence Research Board Fuels Laboratory in the Department of Chemical Engineering, University of Toronto, was responsible for the supply and measurement of additions of hydrogen sulphide to the town gas used for the engine trials.

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THE OXIDATION, IGNITION, AND DETONATION OF FUEL VAPORS AND GASES

XV. THE CONCENTRATION OF FINELY DIVIDED CARBON IN TOWN GAS-AIR MIXTURES REQUIRED TO INDUCE SEVERE KNOCKING COMBUSTION¹

By R. O. KING², E. J. DURAND³, AND A. B. ALLAN⁴

Abstract

When using gaseous fuels for the C.F.R. engine, the lubricating oil decomposed to finely divided carbon when the gas was hydrogen and optimum spark advance nearly zero. When town gas was used, optimum spark advance varied from 85 to 15 degrees of crank angle, according to mixture strength, and the lubricant yielded carbon of the hard adherent graphitic variety. When using an L head engine having a combustion chamber with a large surface-to-volume ratio and with the spark plug so placed that optimum spark advance for town gas was approximately half that required with the C.F.R. engine, no appreciable carbon deposit of any variety was obtained. Conditions were therefore such that knocking combustion observed on adding finely divided carbon to the gas-air mixture was not caused to any appreciable degree by carbon derived from the lubricant. It was then found on adding carbon, as graphite dust, at a measured rate to the entering mixture, that approximately 0.3 mgm. in the end gas caused a knock intensity of the degree required to reduce brake horsepower by from 10 to 14%.

Introduction

The experiments described in this Part were made in the course of an investigation of the factors which have hitherto prevented the use of fuel gases in Otto cycle spark ignition engines at other than economically low compression ratios. The experiments deal especially with nuclear ignition which is of interest in respect of the ignition and explosion, in any circumstances, of mixtures of air with combustible gases or vapors.

The investigation was begun with hydrogen and experiments, Part V (4), demonstrated that the gas could be used in any proportion in mixtures with air at a compression ratio as high as 10 : 1 if it were not impregnated with finely divided carbon derived from pyrolysis of the lubricating oil. It was expected, therefore, that finely divided carbon would be formed when town gas containing hydrogen in a concentration of nearly 50% was used in the engine and that consequent nuclear ignition would again be obtained. It was found, however, as a result of experiments made accordingly and described in Parts XII (2) and XIII (3), that the carbon residue in the combustion chamber was of the hard and adherent graphitic type. There was little if any evidence of the finely divided variety having been formed and a compression ratio of 12 : 1 was used without the occurrence of nuclear ignition.

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The other experiments described in this Part were made with the Armstrong-Whitworth knock testing engine (1) and the results differed from those obtained with the C.F.R. engine in that no appreciable amount of carbon of any variety remained in the combustion chamber.

The experimental results are interpreted as showing why the oil used to lubricate the pistons of internal combustion engines may or may not leave a carbonaceous deposit in the combustion chamber and why a deposit may be of the finely divided or the adherent graphitic type.

The conditions in which the lubricating oil left no carbon in the combustion space having been ascertained, it became possible on adding finely divided carbon to the gas-air mixture at a measured rate to determine the concentration required to cause nuclear ignition and consequent combustion knock of the intensity required to reduce power by a measurable amount.

Experimental Arrangements and Methods

The Engine

A desirable feature of the Armstrong-Whitworth engine is that the detachable head facilitates the inspection or removal of carbonaceous or other deposits that may have collected in the combustion chamber or adhered to the surfaces. The disadvantages of the engine are that the maximum designed compression ratio is 8:1 only and that the attainable mean effective pressure is low as compared with that of the C.F.R. engine.

The essential features of the combustion chamber are illustrated by Fig. 1. The plunger *P* is adjustable by a screw to vary compression ratio over the

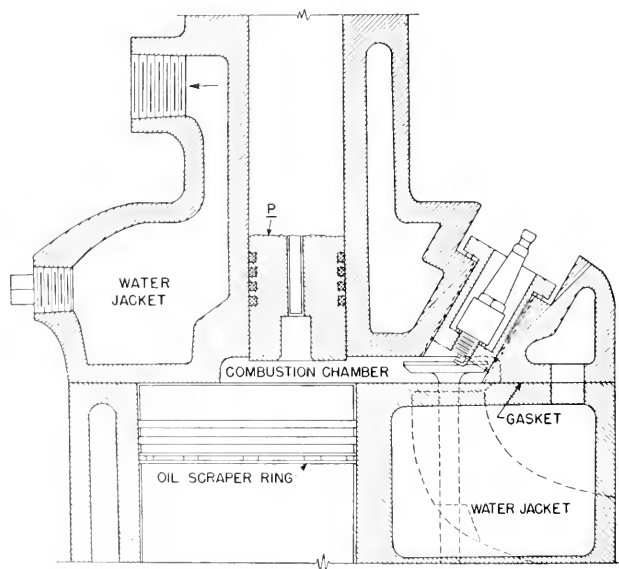


FIG. 1. Combustion chamber arrangements—Armstrong-Whitworth engine.

range 4 to 8 : 1. The higher value of 9 : 1 used for the experiments presently described was obtained by lowering the plunger to project $\frac{1}{8}$ in. into the combustion space, by reducing the volume of the spark plug hole, and by using an extra-thin, $\frac{1}{64}$ in. asbestos composition cylinder head gasket.

The cylinder diameter is $2\frac{7}{8}$ in., the stroke $3\frac{1}{2}$ in., and the stroke volume 22.7 cu. in. The engine and a direct connected swinging field electric dynamometer are mounted as a unit on a cast iron bedplate. The engine was designed originally for the knock rating of fuels but became obsolete on the universal adoption of the C.F.R. engine for that purpose.

Lubrication and Carbon Deposits

It was necessary for the experiments that excess lubricating oil should not pass the piston and that the cylinder head gasket should be tight enough to prevent water or steam entering the combustion space. Some difficulty was experienced in overcoming the evils. The oil difficulty disappeared on replacing the lowest of the three pressure rings by an effective scraper ring fitted in a groove widened from 0.125 in. to 0.110 in. to receive it and on replacing the remaining pressure rings by new ones of a superior design. Water leakage was stopped, in spite of the extremely thin gasket, by scraping the surfaces of the cylinder head and block to an approximate surface plate flatness.

Method of Admitting Finely Divided Carbon, as Graphite Dust

Mechanical methods were tried, beginning with a screw feed stoker design as mentioned in Part V (4). All were defective for the principal reason that induction oscillations made it difficult to govern the rate of feed by mechanical means. It was decided finally to make use of the oscillations to assist in picking up and feeding the dust into the combustion chamber. The device

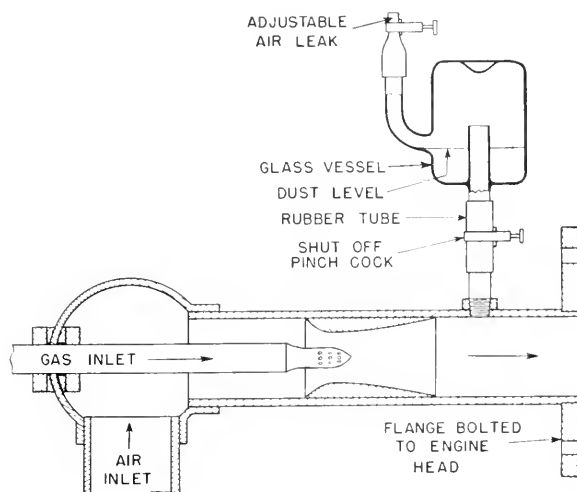


FIG. 2. Device for adding graphite dust to the gas-air mixture.

is fitted to the induction pipe between the carburetor and the engine illustrated by Fig. 2. It comprises a glass vessel with a central side pipe for the admission of the oscillations from the induction pipe and a filling tube at one side. The device is set in operation by fully opening the lower pinchcock, and the rate at which dust is picked up and carried into the combustion chamber can be varied by adjusting the pinchcock at the top of the side tube to provide a small air leak. The vessel is filled with dust to the level shown by the illustration before taking an observation, and the air oscillations act to remove dust at a rate depending on the size of the air leak. The rate is substantially uniform if not more than a total depth of about $\frac{1}{8}$ in. of dust is removed before refilling. The vessel can be refilled without altering the size of the air leak. The regularity of the action is no doubt due to the magnitude of the oscillation remaining constant when the engine speed is unchanged, and the mixture supplied at constant pressure, no throttle being used.

Particulars of Toronto Town Gas

Analysis of Toronto town gas is carried on continuously by the Consumers' Gas Company. The composition determined at the time of the experiments is given below,—

TABLE I
COMPOSITION OF TORONTO TOWN GAS

Constituents	Percentage volume
Hydrogen	47.5
Carbon monoxide	21.3
Methane	12.3
Nitrogen	7.8
Carbon dioxide	4.6
Ethylene	3.9
Ethane	1.1
Benzene	1.0
Oxygen	0.5

The gas contains a trace of organic sulphur not exceeding 10 to 15 grains per 100 cu. ft.

Hydrocarbons constitute a relatively small proportion of the gas and with the exception of the ethylene present in very small concentration are of the type to resist pyrolysis to finely divided carbon even at the temperature of the end gas, that is, they are of the nonknocking variety.

The higher calorific value determined by calorimeter in the Gas Company Laboratory was 467 B.t.u. per cu. ft. at 60° F. and 30 in. of mercury. The lower value, by calculation, was 424 B.T.U. per cubic foot and the density 0.0109 lb. per cubic foot.

The rate of gas supply to the engine was measured by a standard dry meter fitted with a special dial for accurate reading and calibrated by the Consumers' Gas Company.

Experimental Results

Performance Data for the Armstrong-Whitworth (A-W) and C.F.R. engines

Performance data for the two engines were obtained by trials in like conditions for the purpose of facilitating comparison of later experimental results. The trial conditions were, speed 800 r.p.m., jacket coolant 212° F., air and gas at laboratory temperature, and compression ratio 9 : 1.

The value assigned to the compression ratio is based on a measurement of the clearance volume, but even if measurement be correct the *compression pressure* will be less than the correct corresponding value to an extent depending mainly on the amount of leakage past the piston, valves, and cylinder head gasket. The maximum compression pressure for the A-W engine in the conditions mentioned above, taken immediately after running under power, was 207.5 lb. per sq. in. when atmospheric temperature was 85.8° F. and pressure 29.69 in. of mercury. The comparable compression pressure

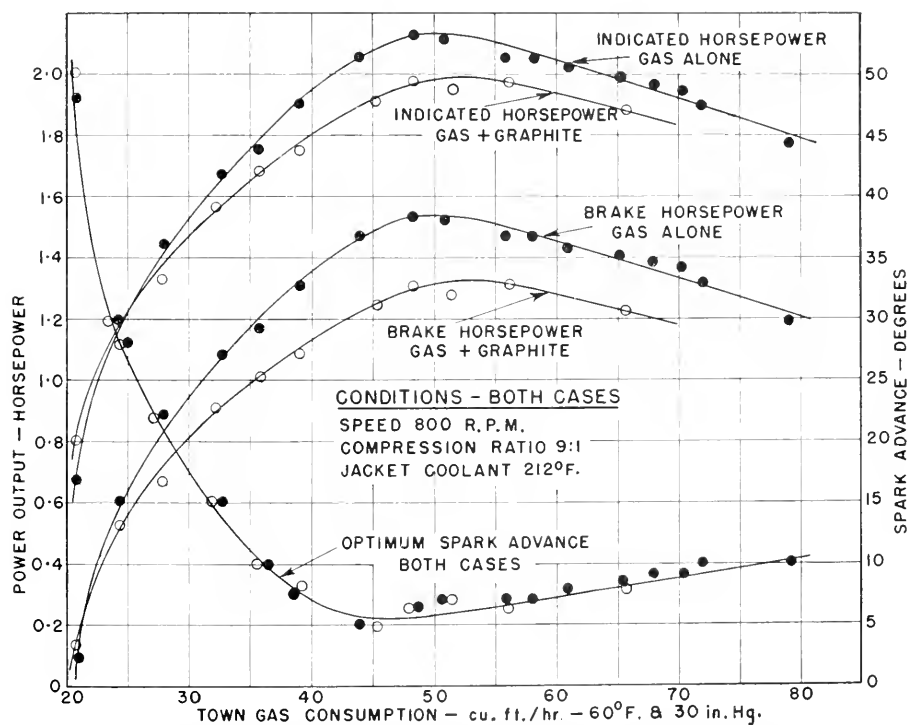


FIG. 3. A-W engine trial results showing variation of optimum spark advance with mixture strength and the reduction of brake and indicated horsepower due to severe knocking combustion induced by graphite dust.

The A-W engine was 209.0 lb. per sq. in. when atmospheric temperature was 60° F. and barometric pressure 25.8 in. of mercury. The small difference of 1.5 lb. per sq. in. in favor of the C.F.R. engine can be accounted for in part by the latter atmospheric temperature and higher pressure and in part by the piston being fitted with three pressure rings instead of the two of the A-W engine. Moreover, there is always a possibility of leakage past the cylinder head gasket of that engine, whereas the C.F.R. engine is constructed with the cylinder head and barrel in one piece, and a jointing gasket is not required.

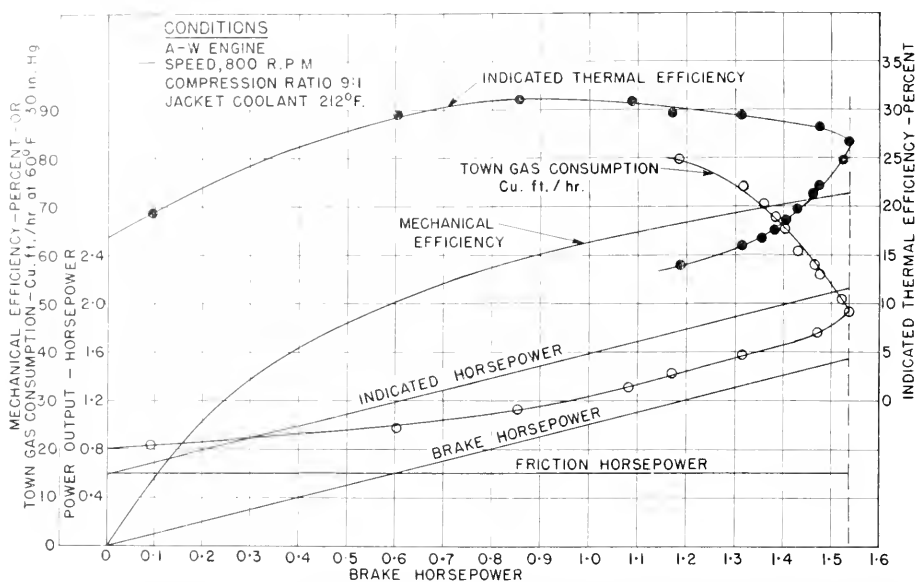


FIG. 4. A-W engine trial; collected results showing especially that indicated thermal efficiency reaches a maximum at 55% of full load and then diminishes as mixture strength is weakened to reduce power.

Performance data for the A-W engine are given in some detail by the graphs of Figs. 3 and 4. The similar data for the C.F.R. engine need not be given in detail, the essential difference between the performances of the two engines being shown by the graphs of Fig. 5. They show that indicated mean effective pressure for the C.F.R. engine attained a value of 126 lb. per sq. in., the corresponding indicated thermal efficiency being 33%. The similar values for the A-W engine were 92 lb. per sq. in. and 27%. The indicated thermal efficiencies attained at the mixture strengths for maximum economy were 39.5% for the C.F.R. and 31.0% for the A-W engine.

The inferior performance of the A-W engine is attributed, in accordance with experiments made by Ricardo (6, p. 203), to the relatively large surface-to-volume ratio of the combustion chamber. The ratio is usually calculated on the basis of the piston being at top dead center. The effective ratio is however that calculated for the position of the piston when combustion is

appreciable. That would be at about 10 crankshaft degrees after passage of the spark. On this basis the surface-to-volume ratio is 7.6 for the A-W and 3.1 for the C.F.R. engine, the ratios being taken for piston positions at maximum thermal efficiency when spark advance is 50° for the C.F.R. and 32° for the A-W engine.

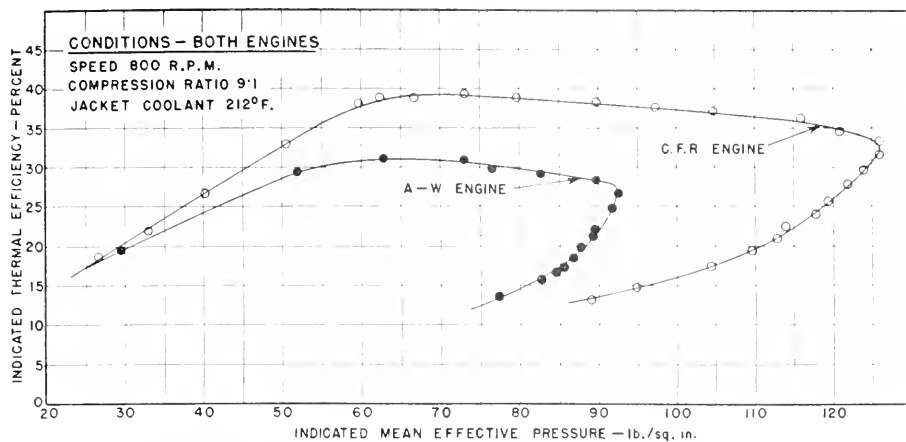


FIG. 5. Relative performances in terms of indicated thermal efficiencies and mean effective pressures of the C.F.R. overhead valve engine and the A-W, L head side valve engine.

Spark Plug Position and Optimum Ignition Timing

Optimum ignition timing varies with mixture strength and was determined by a separate series of experiments as described in Part XII (2, p. 138). The values so obtained for the A-W engine as given graphically, Fig. 3, are much less than values obtained similarly for the C.F.R. engine. At maximum power, optimum ignition timing required a spark advance of 7° for the A-W and 15° for the C.F.R. engine. At minimum power, zero brake horsepower, optimum ignition timing for the A-W was 50° spark advance and 85° for the C.F.R. engine. The somewhat remarkable difference is attributed to the difference in spark plug position. The spark plug of the A-W engine is situated between the side-by-side inlet and exhaust valves and close to them. Thus the spark passes and flame propagation begins in what is substantially freshly admitted combustible mixture that has been heated by contact with the exhaust valve as well as by compression. The spark plug of the C.F.R. engine is situated as far as space permits from the inlet and exhaust valves which are as widely separated as space permits. Thus on the passage of the spark, flame propagation must occur in a mixture diluted to the maximum possible extent with residual exhaust gas, consequently an unusually large advance is required for optimum ignition timing, especially when weak mixtures are used. The attainment of 100% quality control when using the standard ignition system is attributed to the advantageous position of the spark plug.

Combustion Chamber Cleanliness

It was of importance to determine if the experimental arrangements were effective to prevent the accumulation of loose carbon in the combustion space. A trial was run accordingly at maximum power for a period of 92 hr., not continuously. The lubricant was composed of commercial acid-refined hydrocarbon oils blended in the laboratory to provide an S.A.E. 30, viscosity grade. The engine ran for the period without developing combustion knock, and occasional inspection made after removing the engine head showed that carbon was not accumulating in the combustion chamber. At the end of the 92 hr. running time there was a trace only of adherent carbon as a narrow ring around the periphery of the piston and a corresponding faint ring of adherent carbon on the flat part of the head adjacent to it at top dead center. The faint ring of carbon was no doubt due to oil thrown from the edge of the piston as the motion reversed at top dead center. There was also a slight deposit of adherent carbon adjacent to the inlet valve. Otherwise the chamber was clean.

Rate of Admission of Graphite Dust and Consequent Knock Intensity

Graphite instead of carbon dust was used for the experiments, in the expectation, based on earlier experiments, that it would be the more likely to remain dispersed in the gaseous mixture instead of clinging to surfaces and accumulating in the combustion chamber.

The graphite dust, grade No. 2301, was supplied by the Canadian National Carbon Company Limited and consisted of a mixture of "impalpable" powder and larger particles that had passed through a 200 mesh to the inch sieve. The grade is that commonly used in iron foundries for dusting on green sand molds.

Knock intensity is a relative term and the C.F.R.-A.S.T.M. method of defining it in terms of the Octane Scale is unsuitable for use with a non-knocking fuel such as town gas, and a practicable method seemed to be to admit the graphite dust at a constant rate and to determine the consequent degree of knocking combustion in terms of the resulting drop in power and thermal efficiency. What can be described in general terms as steady severely hard knock was obtained when the graphite dust was admitted at the rate of 1.3 oz. per hr. which at the engine speed of 800 r.p.m. is 1.5 mgm. per induction stroke.

The engine performance in terms of brake and indicated horsepower is shown by the graphs of Fig. 3 for gas alone and for gas plus graphite dust admitted at the rate mentioned. The severe knocking combustion induced on adding the dust was accompanied by a decrease in B.H.P. of from 1.54 to 1.32, or 14%, and an increase in gas consumption of from 50 to 53 cu. ft. per hr.

Effect of the Knocking Combustion on Thermal Efficiency

Indicated and brake thermal efficiencies based on the lower heating value (L.H.V.) of 424 B.t.u. per cu. ft. at 60° F. and 30 in. of mercury for the town gas are given by the graphs of Fig. 6. The graphs showing efficiencies when

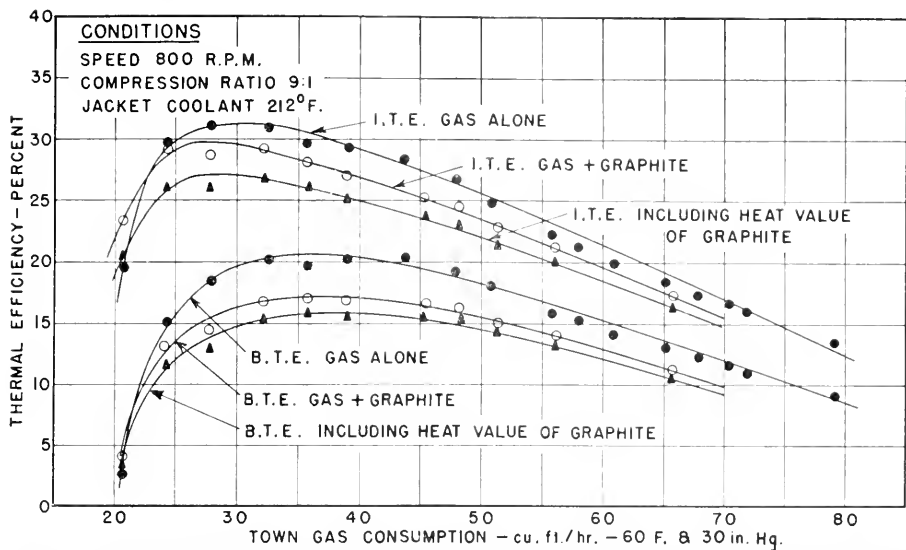


FIG. 6. A-W engine trial; effect of knocking combustion caused by graphite dust to reduce indicated and brake thermal efficiencies.

the heat of combustion of the graphite is taken into account are based on the assumption that it is used with the same thermal efficiency as the town gas. The values shown by the graphs are probably too low because it is doubtful that complete combustion of the graphite occurs when the heat developed can be used with maximum efficiency.

Discussion

It is of interest in respect of the nuclear ignition of gaseous fuels to determine the conditions in which lubricating oil will decompose to the finely divided carbon required to cause the effect.

The absence of finely divided carbon in the combustion space of the A-W engine cannot be attributed to acid-refined oil having been used because a similar result was obtained on using a high grade solvent refined oil or a nonhydrocarbon base synthetic oil for equally long periods of running. It remains, therefore, to consider the combustion conditions in which the finely divided carbon is or is not formed.

When hydrogen alone was used as the fuel for the C.F.R. engine a deposit of fluffy carbon having the appearance of lampblack built up in a few hours

running with the object of igniting the hydrogen-air mixture; Part V (4). The engine was lubricated with a solvent refined oil.

When town gas alone was used in the C.F.R. engine, the residue from the solvent refined oil was the hard graphitic type of carbon, and nuclear ignition was not obtained even at a compression ratio of 12 : 1, Part XIII (3). When town gas was used alone as the fuel for the A-W engine, there was no residue or finely divided carbon in the combustion space and an almost inappreciable amount of the adherent variety, even after 50 hr. running.

The variable factors affecting combustion in the engines were spark advance and the surface-to-volume ratios of the combustion chambers of the C.F.R. and the A-W engines. The effect of these factors on carbon formation will now be discussed.

Spark advance determines the time of exposure of the oil film on the combustion chamber surface to the destructive effect of flame temperature. The effect over a period of time would result not only in the drastic decomposition of the oil to carbon and hydrogen but in at least partial conversion of the carbon to graphite. When hydrogen was used as the engine fuel, combustion occurred in a few degrees of crank angle and in some cases optimum spark advance was negative, i.e., the mixture with air was ignited after top dead center. It was solely in these combustion conditions that finely divided carbon was found in the combustion chamber.

Combustion conditions were very different when town gas was used as the fuel for the C.F.R. engine. Then optimum spark advance varied from 8.5 to 15 degrees of crank angle and the oil film was exposed to the destructive effect of the flame for a period many times greater than when hydrogen was used as the fuel. It was in these conditions that the hard adherent graphitic type of carbon was formed.

When the town gas was used in the A-W engine, optimum spark advance varied from 50 to 7 degrees of crank angle and time of exposure of the oil film to flame temperature was approximately half of that in the C.F.R. engine. Furthermore, the relatively large surface-to-volume ratio of the combustion chamber of the A-W engine ensured a lower surface temperature than prevailed in the C.F.R. engine. That is, conditions were such that the lubricating oil could distill off the surface instead of being decomposed to carbon. In any event, conditions in the combustion space of the A-W engine were such that the knocking combustion obtained on adding graphite dust to the gas-air mixture was not caused to any appreciable degree by finely divided carbon derived from pyrolysis of the lubricating oil.

The concentration of 1.5 mgm. of graphite dust per stroke volume shown by the experiments to be required to induce severe knocking in the A-W engine at 9 : 1 compression ratio is equivalent to a concentration of 180 grains per 100 cu. ft. of air at atmospheric pressure. This is a high value

considering that 8 grains per 100 cu. ft. is regarded as a high concentration in a dusty mine (5, p. 1878). It was far in excess of that required for audible knock and was used, as already mentioned, in order to obtain a consequent measurable decrease of power.

The extreme difference between audible knock and the degree used for the experiments, in terms of compression ratio and B.H.P., is illustrated by the graph of Fig. 7, for an experiment with the C.F.R. engine made when

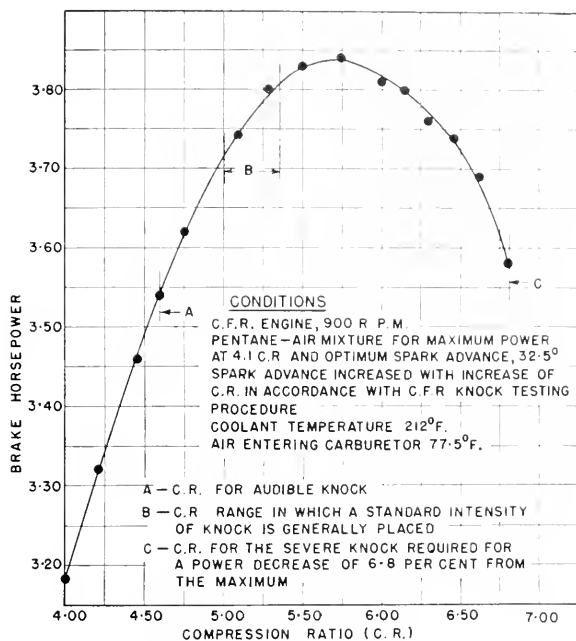


FIG. 7. Graph showing the range of power and compression ratio possible with knock intensity varying from audible to severe.

using *n*-pentane as the fuel. It will be seen that audible knock occurred at a compression ratio of 4.6 : 1; the B.H.P. being then 3.54. The compression ratio could then be raised to 5.27 with a corresponding increase of B.H.P. to 3.8 while the knock intensity did not increase to exceed that commonly used as "standard" and greater intensity could be obtained by raising the compression ratio to 5.62 : 1 before power began to diminish. A still greater knock intensity obtained by raising the compression ratio to 6.8 was required to cause a 9% decrease in power.

Knocking combustion, due to nuclear ignition, requires a suitable concentration of finely divided material in the end gas only. The concentration can be provided accordingly when using hydrocarbon fuels because the decomposition reaction required to provide finely divided carbon can occur preferentially in the end gas in the temperature and pressure conditions

the end of the combustion period. When, however, a nonknocking material such as town gas is used in an engine and the finely divided material is added to the gas-air mixture as admitted, it is necessary to impregnate the gas-air mixture to the concentration required for nuclear ignition of the small end gas which constitutes the end gas.

It is reasonable to assume that the severe knocking combustion obtained when the gas-air mixture supplied to the A-W engine contained 180 grains of graphite dust per 100 cu. ft. occurred when combustion was 80% complete. The weight of dust in the 20% remaining to constitute the end gas would then be 0.3 mgm. at any one knocking combustion.

There seemed to be a possibility that graphite dust on being added to the gas-air mixture in sufficient concentration to cause severe knocking combustion would give rise to ignition by compression. Special experiments were made accordingly but the effect was not obtained at 9:1 compression ratio; jacket coolant being at 212° F., engine speed 800 r.p.m., and the gas-air mixture supplied at room temperature.

Acknowledgments

The experimental work was carried out with the co-operation of Prof. E. A. Allcut, Head of the Department of Mechanical Engineering, University of Toronto, and Assistant Professor W. A. Wallace. The cost of the work was defrayed in part by an extra mural grant from the Defence Research Board, Canada. The National Research Council contributed to the investigation by lending the Armstrong-Whitworth engine. The Consumers' Gas Company of Toronto contributed by lending a newly calibrated special gas meter and by supplying data for the composition and calorific value of the town gas. The Canadian National Carbon Company contributed by supplying the finely divided graphite.

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THE OXIDATION, DECOMPOSITION, IGNITION, AND
DETONATION OF FUEL VAPORS AND GASES

XVI. BENZENE AS A KNOCKING FUEL IN CONDITIONS PROMOTING
THE FORMATION OF FINELY DIVIDED CARBON

By R. O. KING, E. J. DURAND, AND A. B. ALLAN

FUEL OXIDATION, DECOMPOSITION, IGNITION, AND DETONATION OF FUEL VAPORS AND GASES

XVI. BENZENE AS A KNOCKING FUEL IN CONDITIONS PROMOTING THE FORMATION OF FINELY DIVIDED CARBON¹

By R. O. KING,² E. J. DURAND,³ AND A. B. ALLAN⁴

Abstract

Experiments are described which demonstrate that benzene becomes a knocking fuel when used in a spark ignition Otto cycle engine if operating conditions are such that the vapor-air mixture becomes impregnated with finely divided carbon. The carbon was obtained on the impingement of the flame of burning benzene on relatively cool surfaces in the combustion chamber and by the burning of liquid drops dispersed in a combustible vapor-air mixture. The droplets were obtained by wet carburation even when the over-all mixture was weak; the engine being run with low temperature coolant, low temperature air supply, and with the carburetor attached directly to the engine head.

Introduction

The effect of dispersions of finely divided material, even water, to ignite mixtures with air of combustible gases or vapors was described some years ago (6, 7). A theory of nuclear ignition based on the igniting effect of finely divided carbon was described accordingly in Part IV (1) to provide a working hypothesis for a systematic investigation of the detonation which limits the power and economy of Otto cycle spark ignition engines. The investigation has dealt with several aspects of the nuclear theory, and the experimental results have been given in Parts V to XV of a continuing series of papers published in Section F, Canadian Journal of Research.

Knocking combustion as distinct from detonation can be due to ignition of the gaseous mixture by overheated surfaces in the combustion chamber; this effect will be described as surface ignition. Surface ignition may occur prior to spark ignition and is then easily recognized and commonly described as preignition. It may also occur after spark ignition, and the consequent knocking combustion is, in many cases, difficult to distinguish from that due to detonation, especially as the effects may occur simultaneously, Part X (2).

Hydrogen, which cannot be decomposed to carbon, failed to detonate at a compression ratio of 10 : 1 until finely divided carbon was provided in sufficient concentration by pyrolysis of the lubricating oil or added to the entering air, Part V (10).

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Toronto town gas contains hydrocarbons in small proportion, approximately 15 to 20% including the methane. It is therefore not a source of an appreciable amount of finely divided carbon, and the lubricating oil does not yield that variety of carbon when the gas is used as engine fuel, Part XV (3). Detonation was therefore not obtained when the gas was used even at the unusually high compression ratio of 12 : 1 but surface ignition became evident at maximum power on raising the jacket coolant to 351° F. at a compression ratio of 10 : 1, Part XII (1), or to 295° F. at a compression ratio of 12 : 1, Part XIII (5). Detonation was, however, obtained at the relatively low compression ratio of 9 : 1 on adding finely divided carbon as graphite dust to the entering gas-air mixture, Part XV (3).

Benzene is like town gas in being a nonknocking fuel in ordinary conditions of engine operations, surface ignition but not detonation occurring at high compression ratios as first demonstrated by Ricardo (11, p. 115) when running the E 35 engine at 1500 r.p.m., jacket coolant at 140°F., and with heat added to the entering air at the rate of 1500 watts. The antiknock property is due, according to the nuclear theory, to the difficulty of decomposing the substance to carbon by thermal cracking of the end gas in the time available when it is used as an engine fuel. It is possible, however, as shown by the experiments described in this Part, to provide burning conditions in which benzene in any usable concentration in mixtures with air will provide the finely divided carbon required to induce detonation.

Experimental Conditions and Methods

The benzene used for the experiments was reputed to be free of sulphur. Surface ignition was prevented by running the engine at relatively low jacket coolant and inlet air temperatures and at the unusually low speed of 400 r.p.m. in order to reduce power and consequently the temperature gradient required for heat transfer to the coolant.

The C.F.R. knock testing engine used for the experiments was "standard" except that the shrouded inlet valve was replaced by one of the common tulip shaped variety and the arrangement for measuring compression ratios modified to permit measurement of values extending to 13 : 1. Lubrication was by a commercial S.A.E. 30 oil, without additives. The oil in the crankcase was always maintained at approximately 130° F. by the electric heater provided as standard C.F.R. equipment. Inspection of the cylinder and piston on completion of the engine experiments revealed that no damage from defective lubrication had occurred.

Water was used as the coolant and temperature controlled by the thermostatic device described in Appendix (b), Part XIII (5), which made possible the maintenance of a nearly uniform coolant temperature. The water entered the bottom of the cylinder jacket at 85° F. and left the top of the engine head jacket at 90° F.

The air supply was metered by the air box orifice method described in Appendix (a), Part XIII (5), the equipment being set up outside the laboratory building but with pressure leads to a manometer inside, near the engine. The temperature of the air as metered was 32° F. and the relative humidity 58%. The metered air passed through 20 ft. of 3 in. bare steel pipe in the warm laboratory and entered the carburetor at a temperature of 67° F. The relative humidity was then 16%.

Carburetion conditions were arranged to ensure that the benzene was present in the mixture with air, at the beginning of compression, in large part as liquid drops. Thus the mixing chamber fitted as standard C.F.R. equipment was removed and the carburetor, without the usual diffuser, bolted directly to the engine head. The benzene then entered the carburetor as a homogeneous liquid jet and it is probable that "spraying" occurred mainly at the inlet valve because of the high mixture velocity necessarily attained. The temperature drop from the inlet to the outlet of the carburetor was from 9° to 15° F. only, indicating that little vaporization had occurred prior to the entry of the benzene into the cylinder.

Ignition Arrangements

Spark advance was set arbitrarily at 30° at 7 : 1 compression ratio. The timing lever was then linked to the movable engine head and advance varied thereafter automatically with compression ratio. Spark advance was accordingly 25° at 13 : 1, the highest compression ratio of the experiments, and 38° at the low compression ratio of 4.8 : 1. The standard C.F.R. ignition system was modified as described in Appendix (a), Part XIII (5), and the spark gap set at the usual width of 0.025 in.

Standard Knock Intensity

The bouncing pin contacts were so adjusted that a mid-scale reading on the knockmeter was obtained for the approximate standard audible knock intensity of earlier experiments; pentane being used as the fuel. The intensity may be described as moderately heavy. Standard intensity of knock was then taken as having been attained with benzene on adjusting compression ratio for mid-scale knockmeter reading. *It was especially noticeable that the audibility of knocking combustion with benzene varied over a wide range while intensity as indicated by the knockmeter reading was "standard".*

Measurement of Power and Efficiency

Brake horsepower was measured by a swinging field electric dynamometer and the indicated value obtained by the motoring method in general use. Corresponding values of mean effective pressure can be obtained by multiplying by the factor 53.1. Corresponding values of indicated or brake thermal efficiency are based on benzene having a lower calorific value of 17190 B.t.u. per lb.

Experimental Results

The experimental results are exhibited by the graphs of Fig. 1, values of the compression ratio for standard knock intensity, brake and indicated horsepower, and brake and indicated thermal efficiency being plotted as ordinates on a base of mixture strength values. The compression ratio for

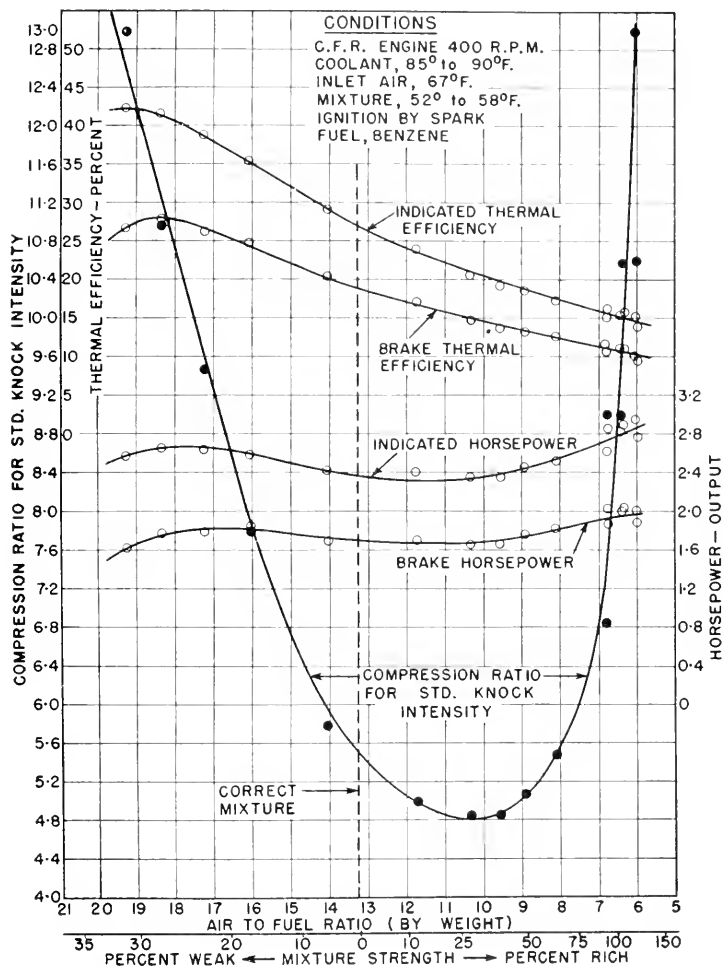


FIG. 1. The variation of standard knock intensity, power, and thermal efficiency with mixture strength when using benzene in conditions to promote nuclear ignition.

standard knock intensity may be regarded as the usable value for the mixture strength at which it is determined and will be referred to as U.C.R. It will be seen by reference to Fig. 1 that it varied from the very low value, for benzene, of 4.8 : 1 for a mixture 30% rich to the high value of 13 : 1 for a mixture 31% weak or 120% rich. Arrangements to use compression ratios higher than 13 : 1 had not been made.

The experiment was begun with a nearly clean combustion chamber and a mixture 30% weak. The U.C.R. as indicated by a mid-scale reading of the knockmeter was then 5.8 : 1 although audible intensity was very light. Mixture strength was increased by steps, and corresponding values of U.C.R. determined, as indicated by mid-scale knockmeter readings, until the maximum measurable value of 13 : 1 for the compression ratio was attained. The mixture was then 120% rich. The audibility of knock increased progressively with increase of mixture strength and at the compression ratio of 13 : 1 was nearly the same as that usually associated with mid-scale knockmeter reading.

The series of measurements was interrupted at a U.C.R. of 10.6 : 1 by the sooting of the spark plug. The part of the combustion chamber, mainly the piston crown, visible through the spark plug hole was then inspected with the aid of interior lighting. The surface was seen to be heavily coated with powdery carbon of the lamp black type.

The experiment was resumed after fitting a clean spark plug and four check observations taken over the mixture range 120% to 90% rich and completed on taking four observations when using mixtures in the order 23%, 31%, 17%, and 28% weak. Audible knock intensity for the mixtures 23% and 31% weak was the same as that observed for very rich mixtures. Intensity diminished progressively for the third and fourth observations but was accompanied by occasional heavy knock. Compression ratio was adjusted for all of the observations to maintain standard knock intensity as indicated by a mid-scale reading of the knockmeter.

Inspection through the spark plug hole on completion of the experiment revealed a thin layer of carbon black on the piston crown. The layer was reduced but not completely removed on continued running of the engine with a mixture 30% weak. Thus it appeared that the layer of powdery carbon on the piston crown formed when running on very rich mixtures diminished in thickness with time of running on changing over to weak mixtures.

It is significant in view of developments to be described later that on switching off the electric spark the engine did not continue to run in the temperature and other conditions of the experiments.

A selection of significant data from the experimental results is given in Table I.

TABLE I
VALUES OF USABLE COMPRESSION RATIO, POWER AND EFFICIENCY,
FOR SIGNIFICANT VALUES OF MIXTURE STRENGTH

Mixture	U.C.R.	I.H.P.	I.M.E.P.	I.T.E.
31% weak	13 : 1	2.56	137 lb.	42%
Correct	5.5 : 1	2.36	125 "	27%
28% rich	4.8 : 1	2.35	125 "	21%
60% rich	5.3 : 1	2.48	132 "	18%
120% rich	13 : 1	2.96	157 "	15%

Discussion

The experiments were carried out in cool engine running conditions in order to prevent surface ignition and simultaneously to promote the burning of benzene in a manner to yield finely divided carbon as soot. The manner in which finely divided carbon is procured remains to be considered.

It is well known that the flame of benzene in an atmosphere deficient in oxygen deposits soot on available surfaces to a greater extent than that of a substance, hexane for example, which contains the same number of carbon atoms in the molecule but more than twice as many atoms of hydrogen. Benzene is thus an undesirable constituent of lamp oil, and readily deposits carbon in the combustion space of an engine when rich mixtures are used. Carbon can however be formed even when oxygen is in excess and combustion complete at the *end* of the period required in an engine, if liquid drops have persisted throughout compression to be present at the *beginning* of the period, when flame is started by the electric spark. The temperature conditions of the engine experiments ensured that the combustible mixture contained sufficient benzene as vapor for spark ignition and sufficient as liquid drops to provide the locally rich mixtures required for the formation of soot. When the mixture in the engine contains an excess of benzene, carbon would be formed on the impingement of the flame on relatively cool surfaces as well as by the burning of liquid drops in the gaseous mixture. When the mixture contains an excess of oxygen, carbon would be formed only by the burning of the locally rich mixture adjacent to the droplets.

The carbon formed as described was always of the powdery lamp black type which could be dispersed into the mixture by the turbulence created by the restriction of the inlet valve, and in the light of the nuclear theory a rational explanation for the characteristics of the detonation observed in cool conditions of engine operation is thus obtained.

Some comment is required in respect of the measurement of knock intensity when using benzene as an engine fuel. It was observed, by King and Moss, in the course of early experiments on "The Measurement of Detonation" (8, p. 220) that the bouncing pin method was not satisfactory if used over a wide range of compression ratios. Although audible knock was not obtained when benzene was used in the experimental conditions, the effect was indicated by the bouncing pin as existing at a compression ratio of 6 : 1 but not at 1 : 1. In another experiment in which there was again no *audible* knock with benzene, the bouncing pin contacts were set just not to indicate any effect. Then on changing to gasoline, knock was plainly audible although no indication of it was given by the bouncing pin. It is evident that the knocking combustion of benzene differs in some way from that of paraffinic fuels. The reason for the difference might be of importance but so far as known has not been ascertained.

Acknowledgments

The experimental work was carried out in the Heat Engine Laboratory of the University of Toronto with the co-operation of Prof. E. A. Allcut, Head of the Department of Mechanical Engineering, and that of Assistant Professor W. A. Wallace, and the cost defrayed in part by an extramural grant from the Defence Research Board (Canada). Experimental assistance was given by Mr. S. Sandler of the Defence Research Board Group in the Department of Chemical Engineering.

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THE OXIDATION, DECOMPOSITION, IGNITION, AND
DETONATION OF FUEL GASES AND VAPORS

XVII. THE NUCLEAR IGNITION OF *n*-PENTANE IN THE C.F.R.
ENGINE AND THE EFFECT ON PERFORMANCE

BY R. O. KING, E. J. DURAND, AND A. B. ALLAN

THE OXIDATION, DECOMPOSITION, IGNITION, AND PETONATION OF FUEL GASES AND VAPORS

XVII. THE NUCLEAR IGNITION OF *n*-PENTANE IN THE C.F.R. ENGINE AND THE EFFECT ON PERFORMANCE¹

BY R. O. KING,² E. J. DURAND,³ AND A. B. ALLAN⁴

Abstract

Temperature and carburation conditions were such that the pentane could persist during compression in part as liquid drops. Finely divided carbon in the concentration necessary for nuclear ignition could then be obtained by thermal cracking at temperatures and pressures attained during the compression stroke. The concentration so obtained was augmented by the carbon formed on burning rich mixtures surrounding droplets of pentane and on the impingement of the flame of such mixtures on the cool surfaces of the combustion chamber. In these circumstances, the engine ran without spark ignition, a standard intensity of knocking combustion being maintained by varying the compression ratio in accordance with change in mixture strength. Indicated thermal efficiencies for mixture strengths varying from 30% weak to 40% rich were, on the average, 83% of ideal values. A maximum value of 53% was obtained for indicated thermal efficiency when using a mixture 60% weak at a compression ratio of 11.5:1, the I.M.E.P. being 98 p.s.i. This surpasses the value of 51.6% accompanied by an I.M.E.P. of 66 p.s.i. obtained with a Diesel engine at 15:1 C.R. and commonly regarded as a record. The experiments provide confirmatory evidence for the nuclear theory of ignition advanced in Part IV and indicate that autoignition by compression, in general, is a nuclear effect arising from a decomposition reaction.

Introduction

The finely divided carbon giving rise to detonation when benzene was used as an engine fuel was formed by the burning of rich mixtures after flame had been initiated by a spark, Part XVI (2). Thus detonation in a particular combustion period could be attributed to the igniting effect of carbon nuclei which had been formed during prior periods, an essential condition being that the carbon is of the powdery form, capable of being dispersed in the combustible mixture by the entering turbulence. The engine would, therefore, not run without spark ignition because an igniting concentration of finely divided carbon was not obtainable in the time available by decomposition (cracking) of the benzene at the temperatures and pressures attained during the compression stroke.

Normal paraffins are principal constituents of "cracking stock", whereas cyclic compounds such as benzene are final products and, in the cracking process, the paraffins yield some proportion of carbon at temperatures and pressures lower than those attained during the compression stroke of an engine.

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The experiments described in this Part were made in the conditions most favorable for the formation of finely divided carbon during the compression stroke. Pentane was used as the fuel and although it is more resistant to cracking than higher members of the paraffin series, compression ignition was obtained at a piston position such that the engine would run without spark ignition at compression ratios varying from 6.8 to 12:1. Performance in terms of indicated thermal efficiency and mean effective pressure was equal to or superior to that obtained at comparable compression ratios with spark ignition or Diesel operation.

Experimental Arrangements

The arrangements were, in general, as described for the experiments with benzene (2). The C.F.R. engine was standard except that the shrouded inlet valve was replaced by one of the common tulip type and the limit of compression ratio measurement was extended to 13:1.

The normal pentane was the technical grade as supplied by Phillips Petroleum Co. A lower calorific value of 19,500 B.T.U. per lb. was used for calculations of thermal efficiency as based on the usual dynamometer measurements of power and friction loss.

The jacket cooling water entered at 85°F. and flow was adjusted automatically to limit the temperature rise to 5°F.

The standard mixture heating chamber was removed and the carburetor bolted directly to the engine head. The diffuser was removed from the carburetor to allow the pentane to enter the venturi throat as a completely liquid jet and thence pass into the engine mainly as liquid drops.

The air metering equipment was set up outside the laboratory building in an open shed and the experiments made in midwinter. The air metering temperature remained nearly constant, at 44°F., during the time required for the experiment; the relative humidity was 56%. The temperature of the air rose to 63°F. while it passed to the carburetor inlet through 20 ft. of bare 3 in. steel pipe in the warm laboratory. The relative humidity was then 28% and ice did not form in the carburetor although vaporization of the pentane reduced the temperature by from 47° to 23°F., depending on mixture strength.

The temperature and entry conditions ensured that the pentane remained in part throughout compression as liquid drops. The drops while slowly evaporating would be surrounded by nearly pure vapor. The physical state most favorable for the formation of carbon by the cracking process was thus provided. The relatively low engine speed of 400 r.p.m. used for the experiments provided the "delay period" necessary for the finely divided carbon to attain the concentration required for ignition of pentane vapor - air mixture.

Experimental Results

The C.F.R. engine had been dismantled and cleaned a few days before the experiments were undertaken. The combustion space was, however,

and cleaning with special scrapers and brushes. The engine was then run for 24 hours in order to stabilize temperatures. The inlet air temperature was 62.6°F., jacket coolant 85° to 90°F., speed 400 r.p.m., and compression ratio 7.5:1. The mixture strength and spark advance were adjusted for maximum power.

On completion of the stabilizing run, spark advance was set at the more retarded value of 10° and compression ratio raised until "standard" knock intensity, as indicated by a midscale reading of the knockmeter, was obtained. The intensity adopted as standard was somewhat greater than generally used for routine fuel testing but was well below that of knock limited power. The knockmeter had been adjusted to give a midscale reading for the adopted standard intensity. The engine ran fairly steadily without spark ignition at 7.7:1 C.R. while maintaining standard knock intensity.

It was observed that running became quite steady, with the appearance of continuing indefinitely, on increasing compression ratio to give a knock intensity greater than standard but still less than that at which power reaches a maximum. The intensity adopted as standard had, however, been used for so many earlier experiments that it was decided to continue with it.

Running without spark ignition continued to be not entirely steady over an intermediate weak mixture range but became quite steady for a mixture 53% weak, compression ratio being then 11.3:1. Steady running without spark ignition continued as mixture strength was reduced to 60% weak and compression ratio raised to 11.5:1. That is, especially steady running without spark ignition was obtained at Diesel engine compression ratios.

The experiment was continued but on the rich mixture side, beginning with a mixture 17% rich for which U.C.R. was approximately 7:1. Mixture strength was increased by steps until at 74% rich, U.C.R. attained a value of 12.4:1, approximately the maximum measurable. The engine ran somewhat unsteadily and with variable knock intensity, without spark ignition. Nevertheless, after being stopped it could be restarted without spark ignition, indicating that the unsteady running was due to the amount of residual carbon being variable, as would be expected.

The experiment was completed by observations at nearly correct mixture strength, namely, 5.6% weak, 2.5%, and 5% rich U.C.R. values being 7.7, 7.2, and 6.9:1, respectively. The engine ran smoothly with standard knock intensity nearly constant and without benefit of spark ignition. It will be noted that the steady running on mixtures nearly correct was obtained when the combustion chamber would be expected to contain residual carbon due to previous running on over-rich mixtures. The combustion chamber surface was then viewed through the spark plug hole and, so far as it could be inspected with the aid of interior lighting, was seen to be free of the adherent type of hard carbon and nearly so of the lamp black type.

The experimental results for engine performance are given by the graphs of Fig. 1. Values of mean effective pressure in pounds per square inch are obtainable by multiplying values of horsepower by the factor 53.1. Significant performance data are given in Table I and related values of ideal efficiencies for

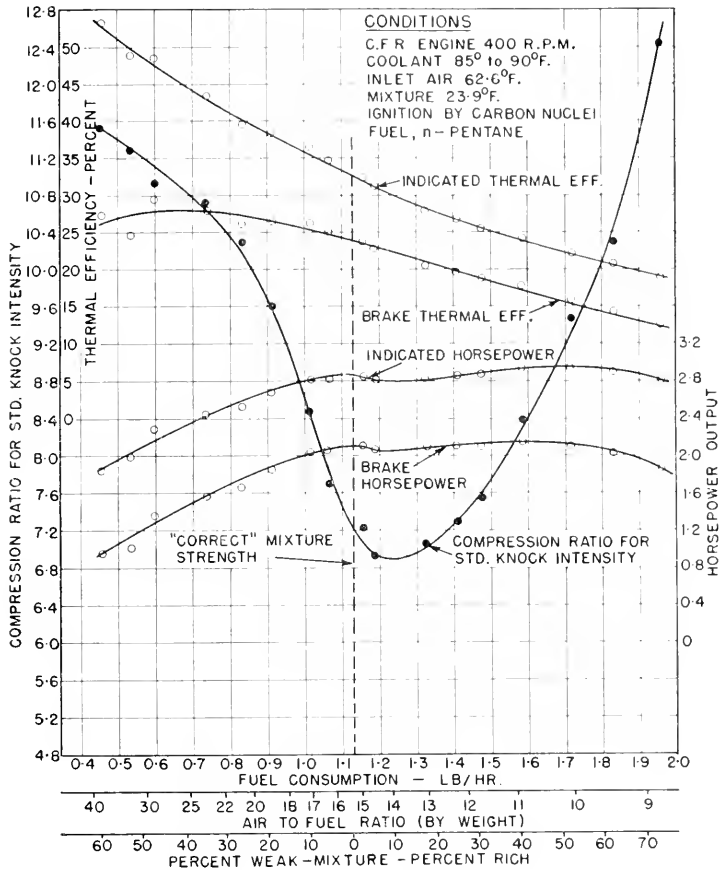


FIG. 1. Graphical presentation of data for power and thermal efficiency, pentane-air mixtures 60% weak to 74% rich.

mixture strengths of from 30% weak to 40% rich are given in the last column of the table. The ideal efficiencies are those calculated by Prof. C. Fayette Taylor, Massachusetts Institute of Technology, from the most recent thermodynamic data and are given, by permission, from unpublished work.

It will be noted that a high performance was obtained in terms of I.M.E.P. It was no doubt due mainly to the high volumetric efficiency obtained in the experimental conditions. The experimental values of indicated thermal efficiency taken over the range of mixture strengths mentioned average 83% of the ideal values given by Taylor.

efficiency for a benzene-air mixture 50% weak is given by Pye as 51.6% at a compression ratio of 10:1. The value obtained for a pentane-air mixture was 48% but at a compression ratio of 11.2:1. The observed value of indicated thermal efficiency for a mixture 60% weak is 33% at a compression ratio of 11.5:1, I.M.E.P. being 98 p.s.i. A

TABLE I
PERFORMANCE DATA FROM FIG. 1

Fuel-air mixture	Usable C.R.	I.M.E.P., lb.	I.T.E., %	Ideal efficiency, Taylor, %
60% weak	11.5:1	98	53	
30% weak	10.4:1	133	42	49
Correct	7.5:1	150	33	42
10% rich	6.9:1	149	30	37
10% rich	8.3:1	157	24	28
75% rich	12.4:1	119	18	

value of 51.6% obtained by Ricardo is quoted by Pye (4, p. 216) as being the highest on record. It was obtained for a direct injection (Diesel) sleeve valve engine at 1300 r.p.m. and I.M.E.P. was 78 p.s.i. as compared with the value of 98 p.s.i. for the carburetor engine.

The comparisons of observed indicated thermal efficiencies with ideal values are given mainly to show that the ability to run the engine on nuclear instead of spark ignition was not accompanied by a sacrifice of performance. The comparisons can be approximate only because the ideal efficiencies quoted were calculated on the basis of an initial temperature of compression of 100°C. The initial compression temperature of the experiments with pentane was lower to an unknown and variable extent. Moreover, the dynamometer method of measuring indicated thermal efficiencies is not regarded as being of a high order of accuracy in the extreme conditions of temperature, and combustion pressures of the experiments.

Discussion

When a carburetor engine runs with the spark ignition switched off, it is generally "hot" and ignition is commonly supposed to be by some overheated surface in the combustion chamber. When, however, a cold engine runs without spark ignition, with unheated air supply and pentane as the fuel, while at the same time developing the power possible at the usable compression ratio, ignition must occur *in* the fuel-air mixture and arise in some way from the heat of compression. In these circumstances, a carburetor engine becomes a compression ignition engine and the mechanism of ignition must be the same as that in a Diesel engine or in a laboratory compression ignition apparatus making a single compression stroke.

The mechanism of ignition will be discussed for the purpose of determining the extent to which experimental results for compression ignition accord with

the nuclear theory of ignition advanced in Part IV (1). The theory is based on the assumption that heating of the fuel-air mixture solely by compression leads to ignition if decomposition of the fuel provides a sufficient concentration of finely divided material. The material would be carbon if that substance is contained in the fuel molecule. The theory was applied to explain the auto-ignition obtained with spark ignition at the high temperature and pressure of the end gas. It is necessary for present purposes to consider how carbon nuclei of ignition can be obtained at the lower temperatures and pressures attained at or near the end of the compression stroke.

Sources of the Finely Divided Carbon Required for Nuclear Ignition in Engines

The carbon is obtainable from one or a combination of four sources, namely (a) pyrolysis of the lubricating oil, (b) the impingement of the flame of rich mixtures on cool surfaces, (c) the burning of rich mixtures surrounding evaporating liquid drops, (d) the thermal cracking of completely vaporized fuel, or (e) the cracking of the nearly pure vapor and rich mixture surrounding liquid drops.

It was shown by experiments with hydrogen, Part V (3), that, starting with a clean combustion chamber, several hours of engine running time elapsed before the finely divided carbon derived from pyrolysis of the lubricating oil accumulated to the extent required to ignite the hydrogen-air mixture. It is assumed therefore that source (a) need not be taken into account when a relatively large supply of carbon is obtainable from fuels containing the substance in the molecule.

Carbon is obtainable from sources (b) and (c) after flame has been initiated by spark ignition. Carbon obtained accordingly may in part remain in the combustion chamber and, on being dispersed by the turbulence of the incoming charge, provide the nuclear concentration required for ignition. The igniting effect may be described as secondary. It provided the ignition required for knocking combustion when benzene was used in cool engine conditions, Part XVI (2), but the engine would not run without benefit of spark ignition.

The finely divided carbon required for primary nuclear ignition at every firing stroke must be obtained from source (d) when the fuel in the mixture with air is vaporized completely or from sources (d) and (e) if vaporization is partial. Higher temperatures and pressures would be required to obtain the necessary carbon from source (d) than from (e). The nuclear concentration from either or both sources, when adequate to start a flame at or near the end of one compression stroke, would be augmented for subsequent strokes by carbon from sources (b) and (c) if rich mixtures were used or if mixtures were weak overall but not homogeneous. The concentration formed per compression stroke from sources (d) and (e) would be expected to decrease with engine speed and with increase in the resistance of the fuel to cracking. It would be expected to increase with compression ratio and with increase of charge pressure which determines the quantity of "cracking stock" admitted per stroke at any particular mixture strength.

3.3. Formation of Nuclear Ignition in the Carburetor Engine

Generally assumed that in the usual circumstances of engine operation, vaporization of the fuel is complete by the end of compression. It is safer to assume that it is complete in the end gas. The concentration of finely divided carbon required for primary nuclear ignition and consequent detonation must then be obtained from source (d), that is, by vapor phase cracking, assuming that the fuel had been vaporized before cracking began. The time required for the accumulation of an igniting concentration is then regarded as a delay period of rising temperature and pressure. It may therefore extend over a time interval beginning before spark ignition and ending with nuclear ignition of the end gas, late in the combustion period. Detonation giving knocking combustion *after* spark ignition is thus obtained and, as is well known, temperature and pressure, that is, compression ratio, must be raised as speed is increased and the delay period shortened in order to maintain a standard knock intensity. Similarly, when the temperature and pressure are increased by increasing compression ratio at constant speed, the formation of carbon nuclei begins earlier and proceeds with increased rapidity. The result is that the delay period moves toward lower compression pressures, nuclear ignition occurs in a larger volume of end gas, and knock intensity increases.

The reason why the C.F.R. engine ran without spark ignition in the conditions of the experiments described in this part is therefore that the delay period began relatively early in the compression period. This was possible because the pentane was admitted mainly as liquid drops and carbon was obtainable from source (e), relatively low temperatures and pressures being required for cracking. The engine speed in addition was relatively low, 400 r.p.m., and, the delay period being lengthened accordingly, the igniting concentration of carbon nuclei was obtained at a piston position such that spark ignition was no longer required. Nuclear ignition timing in the circumstances was adjustable, within limits, by raising or lowering the compression ratio. That the position corresponding to the compression ratio for the standard knock intensity was suitable for a satisfactory engine performance in terms of thermal efficiency and power is apparent from the data of Table 1.

The whole combustible charge becomes the end gas when nuclear replaces spark ignition. The knocking combustion obtained cannot be true detonation, defined as nearly simultaneous ignition throughout the mass of the charge. True detonation, with probably disastrous consequences to the engine, could occur solely if closely packed nuclear centers were distributed uniformly in the combustible mixture. The conditions required could be approached if temperatures and pressures were high enough for vapor phase cracking and if nuclear concentration were increased by supercharging.

It was mentioned earlier that the knocking combustion obtained when using benzene could be attributed to carbon obtained from sources (b) and (c), that is, after flame initiated by a spark had passed through the combustible mixture. When using pentane, carbon was obtainable from the same sources

as well as from sources (*d*) and (*e*), and observed characteristics of the consequent knocking combustion were as would be expected accordingly. The experiments with pentane were begun with a mixture 17% weak and a clean combustion chamber. There was then no accumulation of carbon and the engine ran somewhat unsteadily without spark ignition and with compression ratio adjusted for standard knock intensity. Quite steady running was, however, obtained on increasing the compression ratio and the consequent knock intensity or on using weaker mixtures thus making it possible to increase compression ratio while maintaining standard knock intensity. It would be expected that a change to rich mixtures would increase residual carbon from sources (*b*) and (*c*) and augment the concentration derived from sources (*d*) and (*e*). As shown by the graph for U.C.R., Fig. 1, compression ratio for standard knock intensity reached the limit of measurement when mixture strength was increased from 10% to 70% rich. The somewhat unsteady running obtained when rich mixtures were used without spark ignition is attributed to the difficulty of maintaining a suitable quantity of residual carbon in the physical state required for dispersion by turbulence, throughout the mixture. However, the engine could be started on rich mixtures without spark ignition. Also on changing quickly from rich mixtures to the weaker ones near the correct value, running without spark ignition was quite steady whereas before rich mixtures had been used it was somewhat unsteady, unless the compression ratio were increased to make knock intensity greater than standard.

Conclusion

The "autoignition" obtained after a delay period when gaseous combustible mixtures of fuel vapors and air are compressed in a single stroke apparatus is regarded as a manifestation of nuclear ignition. Similarly the combustion delay period in the direct injection (Diesel) engine is regarded as the time required for the cracking of part of the fuel to yield the concentration of finely divided carbon required for ignition of a vaporized part. It is reasonably possible to go even farther and regard the detonation in tubes, obtained after a short run of flame, as being due to nuclear ignition.

The value of 53% for indicated thermal efficiency was obtained when the mixture was 60% weak and the difference between brake and lost horsepower relatively small. Values measured by the dynamometer method must, in the circumstances, be approximate only. The real interest of the experiments lies in the demonstration of the extent to which spark ignition can be replaced by nuclear ignition in a carburetor engine and the consequent contribution to our knowledge of the mechanism of combustion.

Acknowledgments

The experimental work was carried out with the co-operation of Prof. E. A. Allcut, Head of the Department of Mechanical Engineering, University

of Toronto, and of Assistant Prof. W. A. Wallace. The work was sponsored by the Defence Research Board (Canada). Mr. S. Sandler of D.R.B. assisted with the engine trials. Questions raised by Prof. C. Fayette Taylor of the Massachusetts Institute of Technology in respect of the experimental results were of assistance in clarifying their presentation.

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THE OXIDATION, DECOMPOSITION, IGNITION, AND
DETONATION OF FUEL VAPORS AND GASES

XVIII. THE OPERATION OF A CARBURETOR TYPE ENGINE BY
COMPRESSION IGNITION WITH DIETHYL ETHER
OR ACETALDEHYDE AS THE FUEL

BY R. O. KING, E. J. DURAND, AND A. B. ALLAN

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XVIII. THE OPERATION OF A CARBURETOR TYPE ENGINE BY COMPRESSION IGNITION WITH DIETHYL ETHER OR ACETALDEHYDE AS THE FUEL¹

BY R. O. KING,² E. J. DURAND,³ AND A. B. ALLAN⁴

Abstract

Diethyl ether and acetaldehyde knock violently when used as fuels for carburetor engines in normal temperature and mixture strength conditions. The experiments described in this Part show however that in relatively low temperature conditions both substances can be used at any ignitable mixture strength at compression ratios varied accordingly and that, in the circumstances, ignition can be either by spark or compression. The nuclei required for ignition by compression are believed to be the fog particles which are known to be formed in heated mixtures of air with ether or acetaldehyde prior to explosive ignition.

Introduction

Diethyl ether and acetaldehyde are, without qualification, stated in works of reference to be fuels of extremely low anti-knock value. Thus, Pye (8, p. 85), states that the ether detonates more readily than any other known substance. Egerton, Smith, and Ubbelohde (2, p. 464) report being unable to use acetaldehyde as the fuel for an ethyl knock testing engine because of the violence of knocking combustion.

It was shown, however, by experiments described in Part X (5) that acetaldehyde could be used as the fuel for a C.F.R. knock testing engine, in conditions of an unheated air supply and a relatively low jacket temperature. Ignition was by spark with advance fixed at 10°. The experiments described in this Part show that in similar temperature conditions diethyl ether can also be used as the fuel and that compression ignition can replace spark ignition for either of the fuels.

Experimental Conditions and Methods

Temperature and Humidity of Air Supply

Relatively dry air is required to avoid ice formation in the carburetor when using low boiling point fuels. Suitable air conditioning equipment not being available, it was necessary to carry out the experiments in mid-winter, with the engine drawing the air supply from outside the laboratory. Weather conditions were unfavorable during the greater part of the period, 16 Dec. 1949

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to 7 Jan. 1950, during which the C.F.R. engine was available. Even when it was possible to run without ice forming in the carburetor, temperature and humidity varied during the time required for a comprehensive trial. Every measurement of power and air to fuel ratio was corrected accordingly.

Vapor Lock in Fuel Supply System

Special precautions are necessary to prevent vapor lock in the fuel system when using low boiling point fuels. The effect was avoided by shielding the carburetor bowls and the fuel metering vessels from heat radiation from the engine and by cooling the engine cubicle.

Engine Speed and Charge Density

The engine speed was maintained at 400 r.p.m. by adjustment of load, for all of the experiments. The air supply was unrestricted, the carburetor being bolted directly to the engine head and the standard shrouded inlet valve replaced by one of the ordinary variety. An exceptionally high charge density for a C.F.R. engine was thus obtained, especially in the low temperature conditions of the experiments.

Standard Knock Intensity

The bouncing pin contacts were so adjusted that a midscale knockmeter reading was obtained for a standard degree of audible knock intensity when using pentane as the fuel. The intensity was moderately heavy. The standard intensity of knock was then taken as having been obtained for ether or acetaldehyde on adjusting the compression ratio for a midscale knockmeter reading.

Ignition Arrangements

Spark ignition timing was set arbitrarily at 10° advance and was not adjusted to an optimum value as mixture strength or compression ratio was varied and the engine ran at a low compression ratio without knocking combustion. The engine would, however, run apparently indefinitely without spark ignition on raising the compression ratio to obtain standard knock intensity.

Experimental Results

DIETHYL ETHER

The ether ($\text{C}_2\text{H}_5\text{O}$) boils at 34.6°C. (94.3°F.), at normal atmospheric pressure. The heat of vaporization is 151.0 B.T.U. per lb. The lower calorific value of 14,567 B.T.U. per lb. was used for calculations of thermal efficiencies. The "correct" air to ether ratio by weight is 11.2:1.

Temperature Conditions

Air temperatures outside and inside the laboratory differed little during the experiments. The inside temperature was 47.5°F. at the beginning of the experiments and rose to 50°F. while they were in progress. The outside temperature fell from 46.1°F. to 45.3°F. during the same period. Thus, as

which was drawn by the engine through 20 ft. of 3 in. bare steel pipe. In the laboratory, a compensating effect occurred and the air temperature at the carburetor inlet remained nearly constant at 50°F. The relative humidity of the outside air diminished from 63 to 55% during the experimental period and there was no formation of ice in the carburetor. The temperature of the ether-air mixture entering the cylinder varied from 30.5° to 7.8°F., depending on the rate of supply of ether. Jacket cooling was by an automatic thermostatic control of a water circulation. The temperature of the water was 75°F. at the entrance to the cylinder jacket and 80°F. at the exit from the engine head jacket.

Compression Ratio for Standard Knock Intensity and Corresponding Values of Power and Thermal Efficiency

The values obtained as a result of experiments made over the widest possible range of mixture strength are given by the graphs of Figs. 1 and 2. The compression ratio for standard knock intensity, as indicated by a midscale knockmeter reading, will be described as the "usable compression ratio" and abbreviated to U.C.R. Fig. 1 exhibits values of U.C.R., and corresponding values of brake and indicated horsepower and of brake and indicated thermal

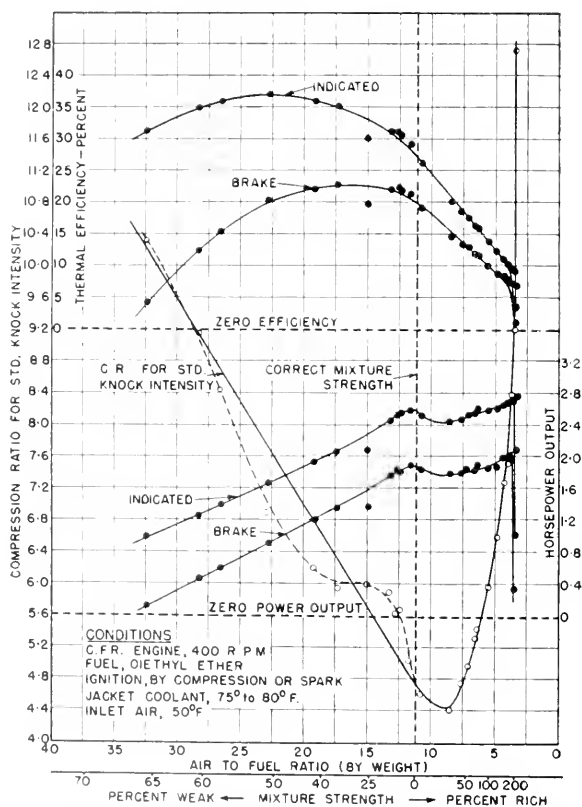


FIG. 1. Diethyl ether, experimental results plotted on a linear base of air to fuel ratio.

efficiency plotted on a linear scale of ether-air ratios by weight and the corresponding mixture strengths in percentages weak or rich as given by a nonlinear scale. The method of plotting expands the graphs on the weak side of the correct mixture strength. They are expanded on the rich side, Fig. 2, by plotting values on a linear scale of rate of ether consumption with corresponding mixture strengths given as percentages of the correct value.

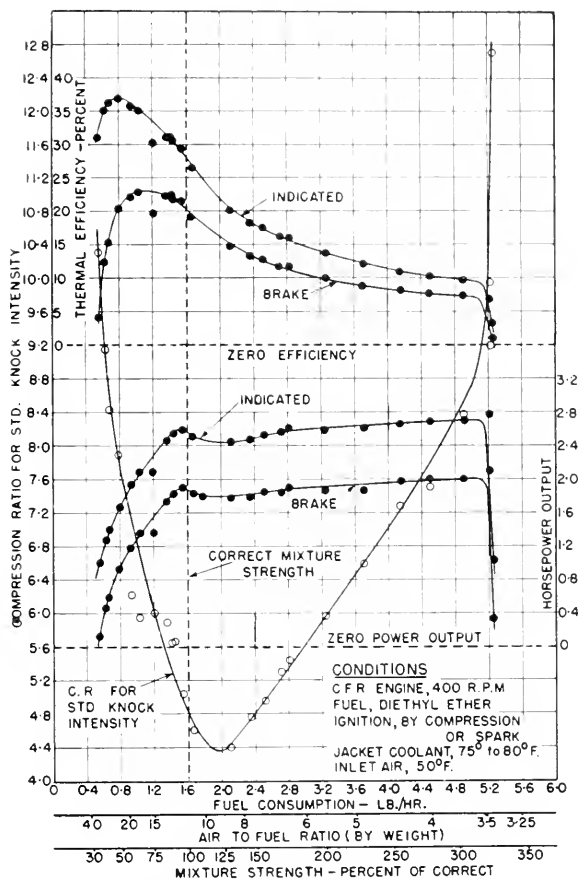


FIG. 2. Diethyl ether, experimental results plotted on a linear base of rate of fuel consumption.

It will be noted that the experimental observations for the U.C.R. of mixtures 10 to 60% weak do not fall on the graph as drawn. The observations indicate that the graph might be drawn as shown by the broken line, Fig. 1. The inflection obtained accordingly was attributed, at first, to experimental error but frequent occurrence in subsequent experiments indicates that it was due to a real effect; the cause being unknown at present.

It was observed in the course of the experiments that at extremely rich or weak mixtures, the audibility of knocking combustion did not correspond with knockmeter readings although standard knock intensity was indicated.

Thus knock was just noticeable at a mixture 66% weak, U.C.R. being 10.3:1. A standard knock intensity was indicated by the knockmeter. A significant feature was that audible knock could be obtained by advancing the spark or by switching it off and raising the compression ratio. That is, when running on compression ignition, ignition timing was set by compression ratio. Somewhat similar effects were obtained with extremely rich mixtures but were always accompanied by heavy and irregular audible knock.

The engine ran steadily on compression ignition at intermediate mixture strengths; the audibility of knocking combustion at the U.C.R. corresponding approximately to the knockmeter reading. The U.C.R. for the correct mixture was 4.8:1 and diminished to a minimum of 4.4:1 for a mixture 20% rich; the corresponding values of indicated thermal efficiency being $27\frac{1}{2}$ and $21\frac{1}{2}\%$ respectively.

Indicated thermal efficiency attained a maximum value of 37% for a mixture 50% weak, U.C.R. being 7.6:1. The value diminished as the mixture was further weakened and the compression ratio raised to maintain a midscale reading of the knockmeter. At a mixture 66% weak, brake horsepower was nearly zero, the U.C.R. 10.4:1 and the indicated thermal efficiency 31%. It appeared that still weaker mixtures could have been used if power had been supplied to compensate, in part, for that lost in overcoming engine friction.

Engine performance on the rich side of correct mixture strength was somewhat remarkable. It is exhibited especially clearly by the graphs of Fig. 2. It will be noted that the engine continued to run and that power, after passing through a minimum value, continued to increase with increase of mixture strength and compression ratio until it dropped suddenly to nearly zero at a mixture just over 200% rich. A similar drop in power which occurred in later experiments was found to be due to loss of compression pressure caused by rotation of worn piston rings until by an odd chance the gaps provided a nearly straight through passageway from the combustion chamber to the crank case.

ACETALDEHYDE

The boiling point of acetaldehyde, CH_3CHO , is 21°C . (69.8°F .) at normal atmospheric pressure. The heat of vaporization is 244.8 B.T.U. per lb. The lower calorific value of 10,550 B.T.U. per lb. was used for calculations of thermal efficiencies. The "correct" air to acetaldehyde ratio by weight is 7.84:1.

Temperature Conditions

The experiments were carried out during a period of falling temperature and rising humidity. The laboratory temperature was 50.5°F . at the beginning of the period and 45.5°F . at the end. The outside temperature was 42°F . at the beginning of the experiments and 36°F . at the conclusion. The relative humidity increased from 42% to 54% during the experimental period but there was no formation of ice in the carburetor. The temperature of the air

entering the carburetor diminished from 54°F. to 47° during the experiment and the temperature of the air-fuel mixture entering the cylinder varied from -7.0° to -8.5°F., depending on the rate of acetaldehyde supply. Water was supplied to the cylinder jacket at a temperature of 85°F. The temperature at the outlet from the engine head jacket was 90°F.

Compression Ratio for Standard Knock Intensity and Corresponding Values of Power and Thermal Efficiency

The experiments were carried out in the manner described for those made with ether as the fuel. The results are exhibited by the graphs of Fig. 3 plotted on a linear scale of rate of acetaldehyde consumption with corresponding mixture strengths given as percentages weak or rich. The acetaldehyde was, in the experimental conditions, usable over a wide range of mixture strengths on the rich side of the correct value but unlike ether the usable range was narrow on the weak side, extending to mixtures no weaker than approximately 25%.

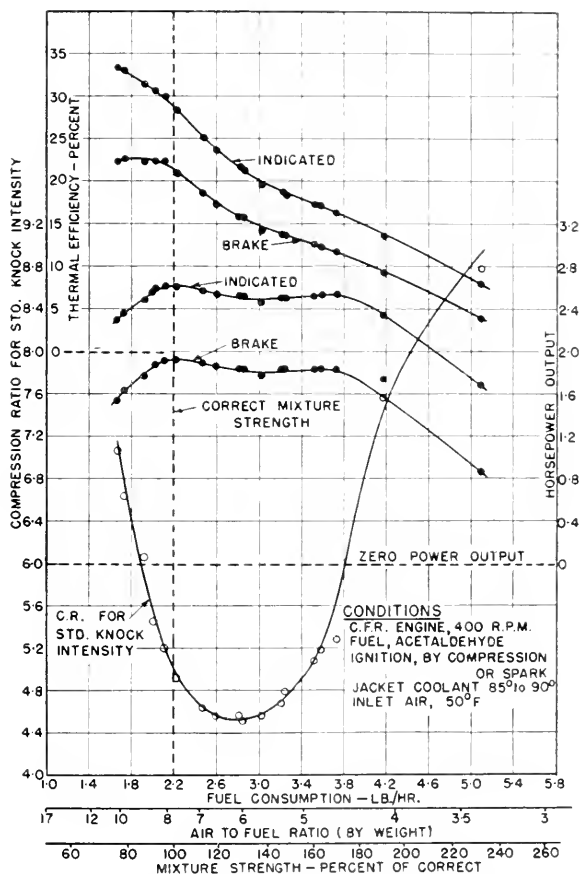


FIG. 3. Acetaldehyde, experimental results plotted on a linear base of rate of fuel consumption.

It was possible to run the engine on compression ignition at any mixture ratio within the range usable with spark ignition if the compression ratio was sufficiently high to be accompanied by audible knock. The running on compression ignition was without irregularity over the mixture range from 10% to 6% to 170% rich and the audibility of knocking combustion could be varied over a wide range by varying the compression ratio. Running became irregular as the weak or rich mixture limit was approached. Compression ignition of mixtures near the rich limit was accompanied by irregular heavy knock.

Discussion

When a carburetor engine continues to run with spark ignition switched off, the necessary fuel igniting effect is commonly attributed to the required high temperature having been attained by a surface in the combustion chamber. The igniting effect, usually described as preignition, is most commonly observed when a hot engine has been operated at maximum power. Thus two means only of ignition are recognized as applying to the carburetor type engine, namely, spark ignition and ignition by overheated surfaces.

It was shown by experiments described in Part X (5) that preignition generally followed the partial oxidation of the fuel to aldehydes, substances which are commonly believed to be ignitable at lower temperatures than the hydrocarbons from which they are formed by partial oxidation. Thus compression ignition of *n*-pentane in the C.F.R. engine occurred at a compression ratio of 6.9:1, Part XVII (6), whereas in the experiments of this Part made in similar conditions of engine temperature and mixture strength, a compression ratio of 4.5:1 only was required to ignite acetaldehyde. It appears, therefore, that early compression ignition, as well as early surface ignition, may be due to aldehydes formed by partial oxidation of hydrocarbon fuels.

The nuclear theory of ignition as stated in Part IV (4) was advanced to account for the autoignition and consequent detonation of the unburned combustible mixture ahead of the flame front in a carburetor engine using hydrocarbon fuels, the nuclei of ignition being finely divided carbon derived from the cracking of the hydrocarbon at the high temperatures and pressures then attained. It was shown by the experiments described in Part XVII (6) that autoignition of the mixture could occur in suitable conditions at the lower temperatures and pressures attained before initiation of flame by a spark; that is, before there was any end gas. The igniting effect was obtained on running the engine at the relatively low speed of 400 r.p.m. and on admitting the fuel, in part, as liquid drops. That is, the conditions were suitable for the liquid phase cracking of the fuel to yield an igniting concentration of finely divided carbon in the time available. The layer of nonadherent carbon deposited on the piston crown in the course of the experiments afforded ample evidence that cracking had occurred.

Tizard and Pye (10) mention that carbon was "thrown down" when ether-air mixtures were suddenly compressed in their machine, to an ignition

temperature of 227°C (440°F). A similar effect was obtained on compressing pentane-air mixtures to an ignition temperature of 300°C (572°F). The temperatures mentioned are minimum values as calculated by Newitt and Townend (7, p. 2962).

The engine experiments of this Part were begun with nearly clean surfaces in the combustion chamber. A deposit of finely divided carbon was visible on water cooled surfaces after rich mixtures containing either acetaldehyde or ether had been used but not after using weak mixtures. If the autoignition of such mixtures be regarded as a nuclear effect, it is necessary to assume that the nuclei were consumed or carried out with the exhaust.

Callendar, when formulating a nuclear theory of ignition (1, p. 21), mentioned co-aggregated molecules as possible nuclei of ignition and initiated appropriate experiments which were carried out by Gill, Mardles, and Tett (3). It was shown by their experiments that explosive ignition of ethyl ether and acetaldehyde in mixtures with air was always preceded by the formation of fog. Ether oxidizes readily to aldehyde and the fog particles, which were so small that an intense beam of light was required to disclose their existence, may be regarded as molecular aggregates of condensation products of aldehyde.

The formation of fog occurs at relatively low temperatures when mixtures of air with ethyl ether or acetaldehyde are heated. Thus it is necessary, if the substances are to be used as engine fuel without excessive knocking combustion, to ensure that mixture temperature at the beginning of compression is exceptionally low. An igniting concentration of nuclei may otherwise be obtained at compression temperatures attained before the completion of the compression stroke, even when the compression ratio is as low as 4:1. An explanation is obtained accordingly for the inability of Ricardo to run the E 35 engine with ethyl ether as the fuel (9, p. 249) in normal operating conditions and for the failure of Egerton, Smith, and Ubbelohde to run the ethyl knock testing engine in similar conditions when using acetaldehyde as the fuel (2, p. 464).

Acknowledgments

The experimental work was carried out with the co-operation of Prof. E. A. Allcut, Head of the Department of Mechanical Engineering, University of Toronto. The cost of the work was defrayed in part by the Defence Research Board (Canada). Observational assistance was given by Messrs. A. J. Wood and M. Hattin, staff demonstrators, and by Dr. D. Aziz and Mr. S. Sandler of the Defence Research Board group in the Department of Chemical Engineering.

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THE OXIDATION, DECOMPOSITION, IGNITION, AND DETONATION OF FUEL VAPORS AND GASES

XIX. OPTIMUM TIMING OF COMPRESSION OR SPARK IGNITION AS DETERMINED BY ADJUSTMENT OF COMPRESSION RATIO; ACETALDEHYDE AND DIETHYL ETHER AS ENGINE FUELS¹

BY R. O. KING,² E. J. DURAND,³ A. B. ALLAN,³
AND E. J. T. HANSEN⁴

ABSTRACT

Acetaldehyde and diethyl ether were used as the fuels for a C.F.R. carburetor type engine run in the cool conditions required to ensure the presence in the charge of liquid drops during compression. Charge density was subnormal and compression ratio was then always adjustable to the value required for maximum power output (the optimum value), without inducing knock of intolerable intensity when using rich mixtures. The spark plugs of the engine were replaced by blind plugs for experiments with compression ignition and both fuels were used with mixture strengths varying from 75% weak, B.H.P. then being zero, to 140% rich. The graphs relating optimum C.R. to mixture strength are of a \bar{W} form with two minimum values of optimum C.R. and an intermediate maximum value. Spark ignition was not effective with mixtures leaner than 40% weak or more than 80% rich. A relatively low engine speed of 400 r.p.m., and the presence of liquid drops in the charge during compression, provided conditions suitable for liquid phase cracking and the compression ignition obtained in the conditions of the experiments is attributed to the effect of nuclei formed accordingly. The experimental results afford evidence of thermal efficiency being affected adversely by the loss during compression of the heat required by the endothermic cracking reaction which produces the nuclei required for compression ignition.

INTRODUCTION

The experiments with acetaldehyde and diethyl ether described in Part XVIII (5) were made with a cool engine, wet carburetion, and normal charge density. Spark ignition was fixed at 10° advance and on adjusting compression ratio to obtain a standard knock intensity, as indicated by a bouncing pin meter, the engine would run with the spark switched off and with no appreciable change of power output.

The term "compression ratio" will be replaced hereafter by the initial letters C.R.

When using a particular mixture strength and continuously increasing C.R., power output increased to a maximum value and then decreased. An optimum C.R. was thus obtainable at which compression ignition timing was such that maximum combustion pressure probably occurred at the suitable piston position which was shown by indicator diagrams to be approximately 10° to 12° after top dead center, for liquid fuels.

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The optimum C.R. could be determined in the manner described for extremely weak mixtures only. Knock intensity became intolerably severe when C.R. was increased to the optimum value for relatively rich mixtures. Knock intensity decreases with a decrease of charge density and the experiments of this Part were therefore carried out with charge density reduced sufficiently to allow the use of optimum C.R. regardless of mixture strength. Mixtures varying from 75% weak to over 300% rich were used for the experiments but the results obtained with mixtures more than 140% rich are not presently described. Knock intensity varied accordingly but was never intolerably severe.

The bouncing pin was not required in the circumstances and was replaced by a blank steel plug.

Two sets of experiments with acetaldehyde and diethyl ether are described in this Part: one with the three spark plugs of the engine replaced by mild steel blanks, "blind plugs"; the other with one spark plug and ignition timing fixed at 10° advance in order to reduce the number of variables. C.R. was always adjusted for maximum power output which occurs necessarily with optimum ignition timing.

No difficulty was experienced in starting from cold when using either fuel, even when blind plugs replaced the spark plugs, if C.R. were set at approximately half a ratio higher than the optimum value.

ARRANGEMENTS MADE TO PROVIDE THE CONDITIONS OF EXPERIMENT

Wet Carburetion

Vaporization of the fuel in the carburetor was restricted by maintaining the air supply at the relatively low temperature of 50° F. and by removing the diffuser. The standard C.F.R. mixture heater was removed, allowing attachment of the carburetor directly to the engine head. The cooling water entered the cylinder jacket at 95° F. and the rise in temperature was restricted to 5° F. by automatic thermostatic control, as described in Appendix (b) Part XIII (6). These arrangements ensured the presence of a wet mixture at the start of compression and vaporization may not have been completed during compression. Completion would depend on mixture strength.

Air Conditioning

It is necessary in the operating conditions required for wet carburetion that relatively dry air be used in order to avoid the formation of ice in the carburetor throat. Air sufficiently dry was obtained for experiments described in earlier Parts by drawing the supply in mid-winter from outside the laboratory building. Air conditioning equipment provided subsequently made possible the continuation of cool engine experiments irrespective of weather conditions. A lagged 15 imperial gallon oil drum fitted internally with three concentric spiral cooling coils of copper tubing, and with suitable air baffles, was used as an addition to the air metering arrangement described in Appendix (c) of Part XIII (6, pp. 154-155) and incidentally increased the air oscillation damping

capacity. A $\frac{1}{2}$ h.p. Freon-12 air cooled condensing unit and three Alco T.K.O.F. Freon expansion valves, one for each cooling coil, sufficed to maintain an air temperature of approximately 5° F. in the cooling drum while air from the laboratory atmosphere was drawn through it at the rate required by the engine. The cooling coils were always defrosted on completion of a set of experiments. The temperature of the air leaving the drum was raised to 50° F. by an electric strip heater before entering the carburetor. The relative humidity was then 25% approximately and ice was not formed in the carburetor.

The Engine

A C.F.R.-F. 2. engine was used for the experiments. It was fitted with balancing pistons and three spark plugs. It was similar otherwise to the C.F.R. knock testing engine used for experiments described in preceding Parts. The standard shrouded inlet valve was replaced by one of the common variety—a spare exhaust valve. The spark plugs and the bouncing pin were replaced by mild steel blanks, “blind plugs”. An engine speed of 400 r.p.m. was used for the experiments.

Carburetor for Subnormal Charge Density

The standard C.F.R. carburetor was modified to provide the subnormal charge density required for the experiments. Thus the diffuser was removed and the expanding nozzle replaced by a choke tube as illustrated by Fig. 5. The choke tube was curved to discharge the wet fuel-air mixture into the engine head well containing the inlet valve. This arrangement led to greater regularity of engine running than when an expanding nozzle was used and the liquid drops in the fuel-air mixture tended to adhere to the rough surfaces in the induction passage in the engine head. The 9-16 in. throat diameter of the venturi in the standard carburetor is overlarge when the engine speed is reduced from the usual 900 r.p.m. to the 400 r.p.m. used for the experiments of this Part and the reduction in charge density due to the use of choke tubes of relatively small diameter was consequently less than would otherwise have been expected. Thus even with a choke tube of 0.25 in. internal diameter the charge densities, which vary with the boiling points and heats of vaporization of the fuels used, were 62% and 67% of the normal value for diethyl ether and acetaldehyde respectively, at the engine speed of the experiments; the normal value being that obtained when the standard C.F.R. carburetor is used, and volumetric efficiency 85%, as determined by measurement of rate of air supply.

Metering of the Fuel and Air

The standard C.F.R. method of controlling the fuel supply to the engine depends on varying the “head” on a small orifice in the fuel passage leading to the carburetor. Orifices less than 0.010 in. in diameter were required at an engine speed of 400 r.p.m. when extremely weak fuel-air mixtures were used. The flow through the orifices, as used with the C.F.R. method of control, was then unstable. It was found that steady flow at the extremely small

required was obtainable by using a fine adjustment needle valve; fuel supply being from a constant head. The flow was metered by the weighing method. The air supply to the engine was metered by the orifice method described in Appendix (c) Part XIII (6). The acetaldehyde and diethyl ether used as engine fuels were as described in Part XVIII (5).

Spark Ignition System

The standard C.F.R. spark ignition system was found to be unsatisfactory when weak mixtures of gaseous fuels were used at relatively high compression ratios. It was replaced by a special Auto-Lite system suggested by Mr. Chester Cipriani (6, pp. 152-153). The system has been used since for all experiments for which spark ignition was required. Sparks over an inch in length in air at atmospheric pressure were obtainable with the system as used, and spark ignition was obtained in the engine when using fuel gases at a C.R. of 20:1, with normal charge density.

Measurement of Brake and Indicated Horsepower

Brake horsepower was measured by a swinging field direct connected electric dynamometer and the indicated horsepower obtained by adding the lost horsepower as determined by the motoring method. The horsepower lost in friction was reduced as far as possible by lubricating the engine with a low viscosity oil, S.A.E. 10, and maintaining the temperature of the oil in the crank case at 120° F. Measurements of lost horsepower, made later than 12 sec. after firing ceased, were not recorded.

TEMPERATURE CONDITIONS FOR COOL ENGINE EXPERIMENTS

It was possible in consequence of the use of refrigeration to maintain the air supply to the carburetor of the C.F.R. engine at an invariable and relatively low temperature. 50° F. was selected as not being significantly different from the temperatures used for the cool engine experiments described earlier, which were dependent on variable winter air temperatures. It is probable that the use of a relatively low air supply temperature, in conjunction with the carburetor attached directly to the engine head, ensured that even a weak mixture entering the cylinder contained some proportion of the fuel as droplets. The temperature of such a mixture would vary with the nature of the fuel and, in any event, it is indeterminate and measurement was not attempted.

The temperature of the cooling water entering the cylinder jacket was maintained at 85° F. for the cool engine experiments with benzene (3), pentane (1), and acetaldehyde (5). A lower temperature of 75° F. was used for experiments with ether (5) mainly because that substance is reputed to "detonate more readily than any other," (8, p. 85). The flow of cooling water was in all instances regulated automatically for a rise of 5° F. in the jackets. Exceptionally low jacket coolant temperatures were found to be unnecessary for experiments with ether and in order to reduce piston friction and thus increase the accuracy of measurement of indicated thermal efficiency, an inlet temperature of 95° F. was adopted for a new series of nuclear ignition experiments of which those of this Part are the first to be described.

The relation between the coolant temperature and that of the *mean* temperatures of surfaces in the cylinder has been determined by others for some conditions of engine operation. There is, however, no information available concerning the *true* surface temperatures which must undergo extreme cyclic changes and be an important factor in respect of the surface oxidation reactions which in turn influence fuel performance.

EXPERIMENTAL RESULTS

Acetaldehyde

The *B* graphs of Fig. 1 exhibit experimental results obtained when the spark plugs and bouncing pin were replaced by blind plugs, the charge density reduced to 67% of normal and the compression ratio always adjusted to the optimum value. The correct air to fuel ratio for acetaldehyde is 7.84:1 by weight. Mixtures varying from 75% weak to 110% rich were used. *Brake horsepower* was zero with a mixture 75% weak. The air to fuel ratio was then 31.4:1, by weight.

The optimum C.R., lower *B* graph, Fig. 1, decreased from 11.9 to 8.1 as mixture strength was increased from 75% weak to 44% weak but on further

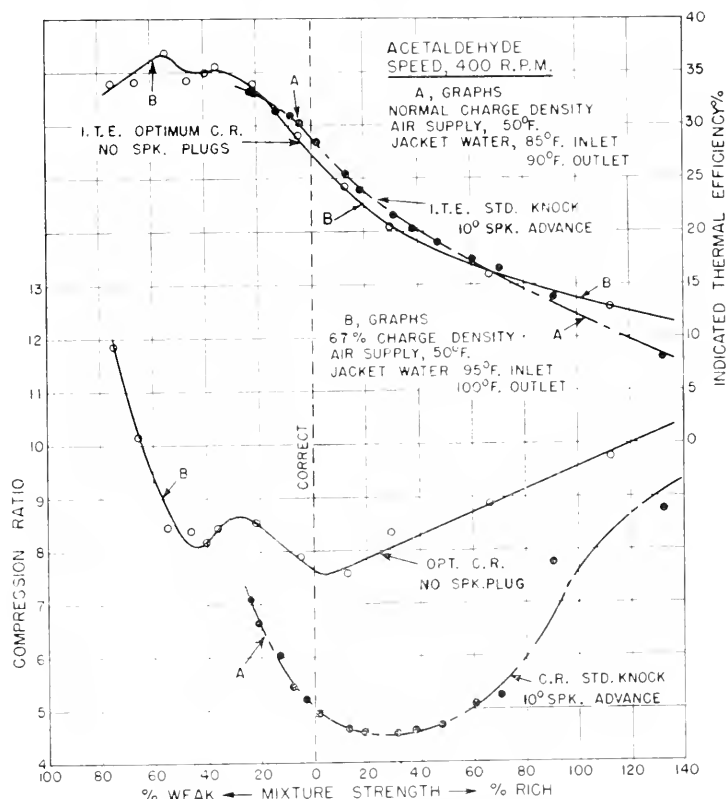


FIG. 1. Acetaldehyde. Results obtained with compression ignition, blind plugs, and reduced charge density compared with those obtained with spark ignition—standard knock intensity, and normal charge density.

15% weak strength to 28% weak, optimum C.R. increased to 8.7, and then decreased to a minimum of 7.5 on further increasing mixture strength to be 5% rich. Thereafter the increase of optimum C.R. with increase of mixture strength was nearly linear. Thus in the conditions of the experiment there were two minimum but unequal values for the optimum C.R. The first, occurring with the mixture 45% weak, is reflected in the graph for indicated thermal efficiency. There is no inflection in the graph in respect of the second minimum.

Combustion was silent when extremely weak mixtures were used but became audible as mixture strength was increased. Light knock occurred with a mixture 40% weak. Knock intensity continued to increase with increase of mixture strength to become medium heavy and somewhat irregular for the correct mixture. It became irregularly heavy and was accompanied by some missing as the mixture strength was increased to be 140% rich. The observations of knock intensity were made when using the optimum C.R.

It is of interest to compare the experimental results described above with those obtained when using normal charge density and always adjusting C.R. for a standard knock intensity as indicated by the bouncing pin meter; circumstances in which the engine would run with or without spark ignition. The broken line, *A* graphs of Fig. 1, have been reproduced accordingly from Part XVIII (5).

It will be seen by reference to Graphs *A* that the earlier experiment was discontinued when the mixture was 25% weak. Both spark and compression ignition were then ineffective and knock exceeded that adopted as a standard intensity as indicated by the knock meter, on attempting to continue with compression ignition by raising the C.R. It was indicated, however, that compression ignition might remain effective as the mixture was progressively weakened while spark ignition would not. This difference between compression and spark ignition was not confirmed until charge density was reduced in order to mitigate the severity of the knocking combustion which occurred with mixtures even as rich as 25% weak. It appears, however, that Graph *A* would have intersected Graph *B* if it had been practicable to carry on with compression ignition after spark ignition had become ineffective, without reducing charge density.

A second significant feature displayed by the experimental results given by the *A* and *B* graphs of Fig. 1 is that the higher C.R. required for optimum compression ignition timing yielded a somewhat lower value for indicated thermal efficiency than was obtained when ignition was with or without spark ignition and C.R. adjusted for the lower value then required for a standard knock intensity. Relative values are given in Table I for mixture strengths in the range commonly used.

It is shown by the data of Table I that with a 15% weak mixture equal values were obtained for thermal efficiency although C.R. was 6.1, *A* graph, and 8.2, *B* graph, whereas according to the ordinary rules of calculation there

should have been a 10% difference. A decrease in thermal efficiency is shown for the correct mixture on raising the C.R. from 5 to 7.6, a change which should have given a percentage increase of 17. The anomalous effect is even greater for the 40% rich mixture for which, on increasing C.R. from 4.6 to 8.3, a decrease in thermal efficiency of 5% was observed, instead of a calculated increase of 22%.

TABLE I
COMPRESSION RATIO AND INDICATED THERMAL EFFICIENCY

Mixture	A Graphs		B Graphs	
	Standard knock intensity normal charge density. With or without spark ignition		Optimum compression ignition timing, 67% charge density blind plugs	
	C.R.	I.T.E., %	C.R.	I.T.E., %
15% weak	6.1	32	8.2	32
Correct	5.0	29	7.6	27½
40% rich	4.6	20	8.3	19

Diethyl Ether

The *B* graphs of Fig. 2 exhibit results of experiments made with ether when the spark plugs and the bouncing pin were replaced by blind plugs, the charge density reduced to 62% of normal, and C.R. always adjusted to the optimum value. The correct air to fuel ratio for diethyl ether is 11.2:1 by weight. Mixtures varying from 75% weak to 140% were used. Brake horsepower was zero with a mixture 75% weak. The air to fuel ratio was then 44.8:1.

The broken line *A* graphs of the figure are reproduced from Part XVIII (5) and exhibit experimental results obtained when using normal charge density and always adjusting C.R. for a standard knock intensity as indicated by the bouncing pin meter, circumstances in which the engine ran with or without spark ignition.

A comparison of Graphs *A* and *B* shows that the inflection in Graph *A* which in the earlier experiment was considered as possibly due to experimental irregularity (5, p. 385) did in fact indicate a real effect which, when using the new method of experiment, became the first of two minimum and equal values of the optimum C.R.; the corresponding mixture strengths being 10% weak and 25% rich respectively. The intermediate maximum value of the optimum C.R. occurred with a mixture 10% weak and was as shown by Graph *B*, 1.75 C.R. higher than the minimum values. A nearly symmetrical *W* form is imparted accordingly to the graph for optimum C.R. over the mixture range 65% weak to 80% rich.

It will be noted that the *A* and *B* graphs, Fig. 2, for the relation between compression ratio and mixture strength, intersect when the mixture is 25% weak and the compression ratio 6.0. On the rich side of the intersection,

efficiency decreases with increase of C.R. This anomalous effect is, though somewhat smaller than was obtained when using acetaldehyde as the engine fuel. On the weak side, a higher thermal efficiency corresponds with the use of a higher C.R. but the relation is not in accordance with known factors. Graph B of Fig. 2, for I.T.E., would be of more nearly conventional form if it were as shown by the dotted line. Too much reliance cannot be placed on the observation made with the mixture 70% weak.

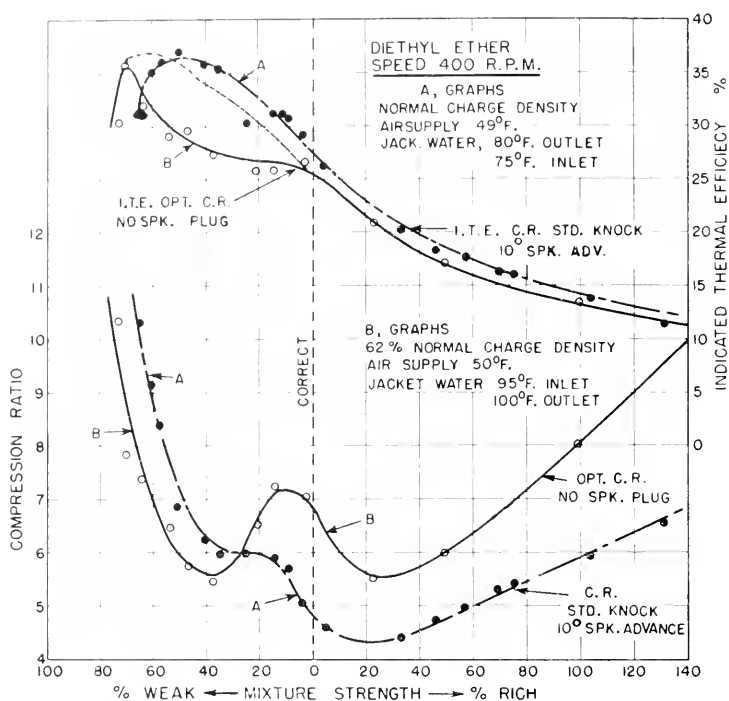


FIG. 2. Diethyl ether. Results obtained with compression ignition, blind plugs, and reduced charge density compared with those obtained with spark ignition, standard knock intensity, and normal charge density.

Combustion was silent when extremely weak mixtures were used. Light knock developed as mixture strength was increased to 40% weak. It continued to increase with increase of mixture strength and to become medium heavy for mixtures approximately correct. The intensity became somewhat variable as between medium heavy, and heavy, with mixtures ranging from correct to 140% rich. Misfiring occurred occasionally. Knock intensity characteristics were, as nearly as could be judged by ear, similar to those observed during the experiments with acetaldehyde although that substance required higher values of the C.R. for optimum ignition timing. The running of the engine with ether as the fuel was noticeably smoother than when acetaldehyde was used.

Acetaldehyde. Results of Experiments with Spark Ignition Compared with Results Obtained with Compression Ignition; 67% of Normal Charge Density

It was shown by experiments described in Part XVIII (5), and reviewed earlier in this Part, that ignition of acetaldehyde air mixture varying from 25% weak to 140% rich would occur with or without spark ignition if C.R. were adjusted for a standard knock intensity. The experiments were made with normal charge density, and spark ignition was always set at 10° advance. Spark ignition failed when mixture strength was leaner than 25% weak. Compression ignition also failed if C.R. were restricted to the value for standard knock intensity.

The results of reducing the charge density to 67% of normal and using the optimum C.R. while retaining spark ignition are exhibited by the C graphs of Fig. 3. Spark ignition was ineffective when the mixture was leaner than 10% weak, but it was possible to continue into weaker mixtures with ignition by compression, always using the optimum C.R., until the mixture became 75% weak and power output zero.

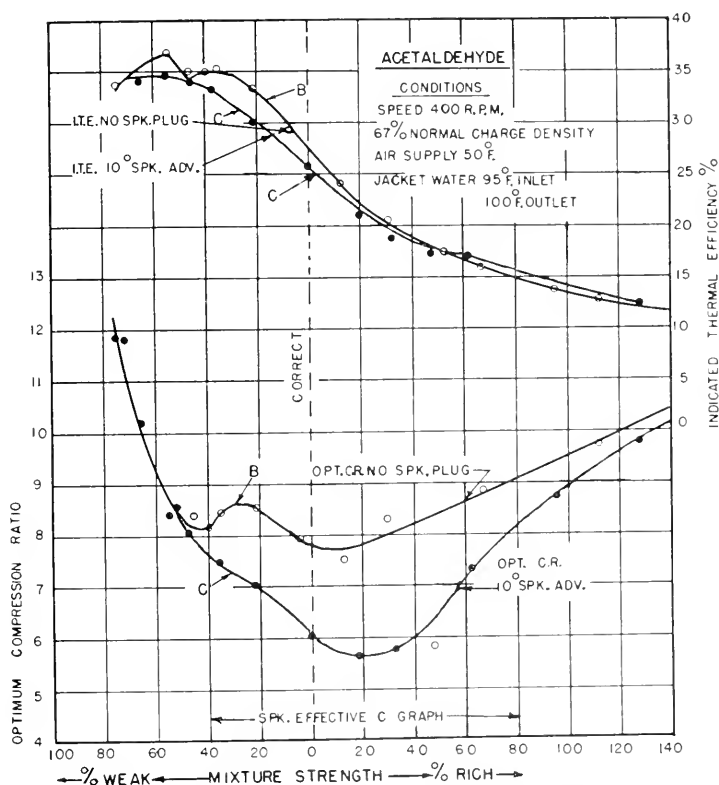


FIG. 3. Acetaldehyde. Results obtained with and without spark ignition and in both cases using optimum compression ratio, reduced charge density, and same temperature conditions.

The A graph was silent with extremely weak mixtures. Knock became audible and very light on increasing mixture strength to 40% weak and became light again even on increasing mixture strength to 80% rich. It became medium heavy for a mixture 110% rich.

The B graphs of Fig. 3 are reproduced from Fig. 1, and exhibit experimental results obtained with charge density 67% of normal, and with blind plugs instead of a spark plug; the optimum C.R. for compression ignition always being used. Graphs B and C thus represent experimental results obtained in like conditions of charge density and engine and air supply temperatures.

Comparing the two graphs, giving the relation between optimum C.R. and mixture strength, it will be seen that for mixtures leaner than 40% weak, the experimental points for both sets of experiments fall on a single line as would be expected in view of spark ignition having become ineffective. It also became ineffective, as already mentioned, when mixture strength was more than 80% rich but the graphs do not then coincide. It is evident that the spark plug introduced an igniting effect not due to the spark.

It is of interest to compare the relation between thermal efficiency and C.R. observed when blind plugs were used with the similar relation observed when ignition was by spark; C.R. being adjusted for optimum ignition timing in both cases. The comparison is made only for mixtures increasing in richness from 10% weak, in part because of spark ignition being ineffective with weaker mixtures. Relevant data from the originals of the graphs of Fig. 3 are tabulated below.

TABLE II
RELATIVE EFFECTS OF COMPRESSION AND SPARK IGNITION ON INDICATED THERMAL EFFICIENCY (I.T.E.) WITH ACETALDEHYDE AS ENGINE FUEL, SAME CHARGE DENSITY BOTH CASES

Mixture	Opt. C.R. (spark)	Opt. C.R. (blind plugs)	I.T.E. (spark), %	I.T.E. (blind plugs), %	% Increase I.T.E.	Calculated inc., %
10% weak	7.7	8.2	33½	35	4.5	2.0
20% weak	7.0	8.5	30	33	10.0	6.3
Correct	6.0	7.8	25½	27½	7.8	9.3
20% rich	5.6	7.8	21	22½	7.2	12.8
10% rich	5.9	8.2	18	19	5.5	12.0

The compression ignition obtained when using blind plugs appears to yield an increase in thermal efficiency for mixtures weaker than correct and a decrease for correct and richer mixtures.

Diethyl Ether. Results of Experiments with Spark Ignition Compared with Results Obtained with Compression Ignition; 62% of Normal Charge Density

The B and C graphs, Fig. 1, exhibit experimental results obtained when charge density was 62% of normal. The B graphs are reproduced from Fig. 2 and give results obtained without spark plugs and with the optimum

C.R. for compression ignition. The *C* graphs give results obtained with one spark plug, spark timing being set 10° advance, and the C.R. adjusted for maximum power.

Comparing the *B* and *C* graphs, giving the relation between optimum C.R. and mixture strength, it will be seen that the characteristics are in general similar to those observed when acetaldehyde was used as the fuel for the

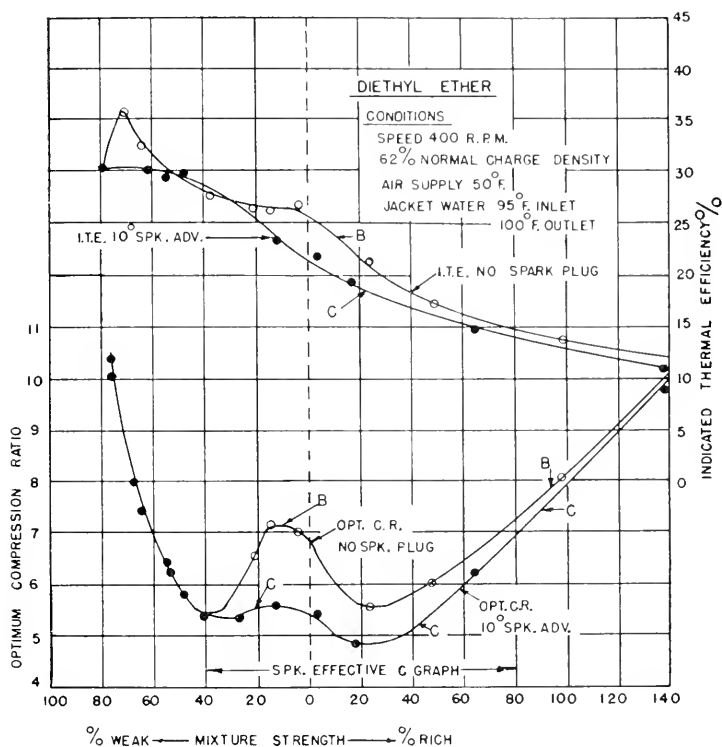


FIG. 4. Diethyl ether. Results obtained with and without spark ignition and in both cases using optimum compression ratio, reduced charge density, and same temperature conditions.

engine. Thus spark ignition failed when the mixture became leaner than 40% weak and the experiment was continued by using compression ignition until the mixture was 75% weak and power output became zero. Spark ignition also failed, as with acetaldehyde, when the mixture became more than 80% rich, and again it was possible to carry on with still richer mixtures by using compression ignition. The *B* and *C* graphs coincide when the mixture is leaner than 40% weak and spark ignition is ineffective but not when the mixture is more than 80% rich and spark ignition again ineffective. It was suggested when describing the similar experiments with acetaldehyde that this rather puzzling phenomenon might be due to the spark plug having an igniting effect independently of the spark. This was found to be so in the course of experiments to be described in another Part. They demonstrate

TABLE III

TABLE III. EFFECT OF COMPRESSION AND SPARK IGNITION ON INDICATED THERMAL EFFICIENCY WITH DIETHYL ETHER AS FUEL, SAME CHARGE DENSITY BOTH CASES

Mixture	Opt. C.R. (spark)	Opt. C.R. (blind plugs)	I.T.E. (spark), %	I.T.E. (blind plugs), %	Observed inc., %	Calculated inc., %
30% weak	5.3	5.7	27	27	0	3.1
10% weak	5.6	7.1	23½	26	10.6	9.5
Correct	5.5	6.8	22	25½	15.8	8.8
20% rich	4.8	5.6	19	21½	13.2	6.9
40% rich	5.2	5.8	17	18½	8.8	4.8

that the ceramic core of an unfired plug, not its points, possesses an igniting effect when ignition is by compression.

Combustion was silent with weak mixtures and as for the spark ignition experiments with aldehyde in similar conditions, it became light only on increasing mixture strength to 80% rich.

The relative effects of compression and spark ignition on thermal efficiency differed from those observed when acetaldehyde was used in that for mixtures ranging from correct to 40% rich the effect of compression ignition was beneficial rather than deleterious. Relevant data are tabulated above.

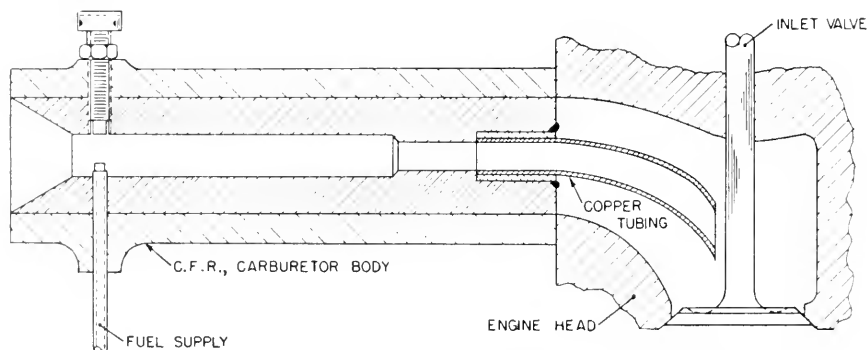


FIG. 5. Carburetor arrangement for experiments with reduced charge density.

DISCUSSION

The novel features of the method of experiments described in this Part are the use of the C.R. for optimum timing of either spark or compression ignition and a subnormal charge density in order to prevent knock intensity becoming intolerably severe on increasing mixture strength from very weak to very rich. The experimental arrangements were otherwise similar to those of the experiments on nuclear ignition described in Parts XVI (3), XVII (4), and XVIII (5). That is, the engine was run "cool" at the relatively low speed of 400 r.p.m. and with wet carburetion in order to facilitate the formation of an igniting concentration of nuclei by liquid phase decomposition or cracking of the fuel

and to reduce the tendency of hot surfaces in the combustion chamber to ignite the combustible mixture or to promote preflame oxidation.

The W form of the graphs relating C.R. for optimum compression ignition timing and mixture strength is in general similar to that described by Campbell as having been obtained when using *pentane* in standard knock rating conditions, see discussion of paper on *Precombustion reactions in the spark ignition engine* by Retailliau, Richards, and Jones (9), Standard Oil Development Co. The especially interesting features of Campbell's experiments were the finding that aldehyde was formed in great profusion in mixtures too weak to be ignited by the spark if C.R. were raised to induce greater than "borderline" knock intensity and that compression ignition occurred on further increasing C.R.

The authors of the paper mentioned above consider that during compression, oxidation precedes decomposition. Their experiments were, like those of Campbell, made with a hot engine; the jacket coolant being maintained at 212° F. and the fuel-air mixture raised to 300° F. before entering the cylinder. It would be expected, therefore, that oxidation of fuel on hot surfaces in the combustion chamber would begin immediately on admission of the charge in the conditions of turbulence induced by the passing of the charge with high velocity through the restricted opening of the inlet valve.

Further experiments on precombustion reactions, carried out in the du Pont Petroleum Laboratory, were described by Pastell (7) six months later. A *motored* engine was used with the jacket coolant maintained at 212° F. and the inlet mixture temperature varied over the range 100 to 400° F. A special feature of the experiments was that manifold air pressures were varied over the range 15 to 75 in. Hg. Both oxidation and decomposition must have occurred during compression in the temperature conditions. Oxidation seems to have been regarded as the predominant reaction because the *heat liberated* is taken into account when discussing thermal efficiency, no allowance being made for the heat absorbed by an endothermic decomposition reaction. The hot engine may be regarded as a heated chamber into which reacting mixture is admitted suddenly and its temperature raised by contact with uncooled surfaces and by compression. It is of interest accordingly that the combustion characteristics described by Pastell are in general similar to those determined by Townend (10) when compressed mixture was admitted suddenly to a heated bomb.

Cold fuel-air mixture was admitted into a cool engine in the experiments of this Part and it is considered that decomposition was the primary reaction and provided the nuclei on which oxidation occurred in the body of the mixture. It is difficult to account otherwise for the profuse formation of aldehyde in extremely weak mixtures, as reported by Campbell, and for the fact that such mixtures can be ignited by the heat of compression but not by a spark. What is thus regarded as nuclear ignition was obtained in the experiments described in this Part, with mixtures 75% weak to 140% rich. The range has moreover been extended at both ends. Spark ignition, on the other

being $\phi = 0.95$ give only over the mixture range 40% weak to 80% rich. It appears, therefore, that recorded limits of inflammability apply solely to homogeneous gaseous mixtures and that the relatively high rate of flame propagation in engines is due in part to the nuclei always present in some concentration.

Pastell, in the reference quoted, mentions three of the several theories advanced at various times to explain detonation. These may be regarded as the survivors. They are in the order given, the Callendar nuclear theory as modified by King (1, 2), the detonation wave theory, and the autoignition theory which is stated to be the hypothesis most generally accepted. The modified nuclear theory as advanced in Part IV (2) was, as stated by Pastell, based on the assumption that detonation of the end gas would be initiated by nuclear particles of carbon. The assumption was made in respect of unsupercharged carburetor engines using paraffinic fuels for which the C.R. seldom exceeds 7:1. The temperature required for nuclear ignition is then attained in the end gas only and when the mixture is approximately correct. Moreover, the required concentration of nuclei can be formed in the time available only in such mixtures and carbon particles are probably the sole type of nuclei capable of persisting until detonation occurs late in the combustion period. In mixtures even 25% weak, flame movement in the absence of nuclei is relatively slow and exhaust valves are liable to some degree of burning. Compression ignition is a different problem. A relatively high C.R. is required for ignition and combustion must be completed soon after top dead center if an acceptable value of thermal efficiency is to be obtained. The ignition process is that of the Diesel engine and maximum thermal efficiency is obtained with mixtures leaner than the weakest which can be used in the spark ignition carburetor engine operated at a relatively low C.R. The experiments of this and Part XVIII (5), were concerned with compression ignition. There is then no end gas and the results indicate that the nuclei responsible for the ignition of *weak* mixtures may be regarded tentatively until further experiments are completed, as aggregates of condensible products of aldehyde (5, p. 389). Thus deposits seen on the piston after long continued running on very weak mixtures were of a resinous appearance and after similar running on rich mixtures, the piston crown was found to be heavily coated with finely divided carbon. It is indicated accordingly that the autoignition obtained by compression was a nuclear effect.

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**THE OXIDATION, DECOMPOSITION, IGNITION,
AND DETONATION OF FUEL VAPORS AND GASES**

**XX. THE ADVERSE EFFECT ON THERMAL EFFICIENCY OF THE
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BY R. O. KING² AND A. B. ALLAN³

ABSTRACT

Autoignition in engines may, depending on compression ratio and the nature of the fuel, occur before, after, or without spark ignition and is due, according to the Nuclear Theory as stated in Part IV, to the heat of oxidation reactions on material particles formed by the cracking of the fuel. Cracking is an endothermic reaction and the consequent absorption of heat in the gaseous phase would be expected to result in a lower thermal efficiency than would otherwise be obtained. The results of experiments with methanol, acetaldehyde, and ether have been used in this Part in an endeavor to verify the validity of the theory. Thus, methanol cannot be decomposed in the engine to the extent necessary for the formation of material nuclei and autoignition was not obtained. Acetaldehyde and ether decompose relatively easily and autoignition occurred at relatively low compression ratios. Corresponding thermal efficiencies are exhibited by a series of graphs which show the extensive deviations from ideal efficiencies observed when acetaldehyde and ether were used as fuels compared with that observed when methanol was used. The deviations are as would be expected taking heat of activation into account and it is indicated that in most cases a pressure wave is required for the nuclear ignition of other than a small volume of unburned mixture remaining late in the period of combustion when the ignition is by spark. The experiments described are in respect of an hitherto unexplored aspect of the nuclear theory of ignition and are to be regarded as preliminary to more detailed ones with hydrocarbon fuels.

INTRODUCTION

The experiments with acetaldehyde and diethyl ether described in Part XIX (6) were carried out with reduced charge densities and with a carburetor type engine operated at relatively low temperatures. It was possible in the conditions to use either spark or compression ignition and to adjust the compression ratio to the value required for maximum power output with any mixture strength without causing an intolerable intensity of knocking combustion. It appeared to be possible, in the circumstances, to determine the effects of the individual limiting factors on engine performance in terms of power and thermal efficiency. Detonation with some fuels and preignition with others are the important factors.

The hypothesis that detonation in a carburetor type spark ignition engine is due to the igniting effect of nuclei formed by decomposition (cracking) of the fuel at the high temperature and pressure attained by the last part of the

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fuel-air mixture to burn was advanced in Part IV (5). This decomposition is an endothermic reaction and the heat absorbed accordingly would be expected to affect thermal efficiency adversely. The adverse effect would be inappreciable if the reaction occurred solely in a small part of the combustible mixture which remained unburnt late in the combustion period. The effect would, however, become greater as the end gas increased in volume with increase of compression ratio and would attain a maximum value when the whole mixture became in effect the end gas.

The idea that an endothermic reaction may occur in the combustible mixture is not novel. The reaction was suggested by Callendar over forty years ago, in a paper on "the effect of size on the thermal efficiency of engines," as possibly one of the factors which prevent air standard efficiency being attained in a real engine (1, p. 226). The possibility does not seem to have been investigated experimentally. Dissociation and the change in the ratio of the specific heats with increase of mixture strength are the sole effects commonly taken into account when calculating the ideal efficiency of a real engine. These effects occur in respect of the products of combustion and on this basis it is solely the expansion ratio which controls thermal efficiency.

If, however, endothermic reactions are taken into account, efficiency may vary also with the liability of the fuel to decomposition by the heat of compression.

When acetaldehyde and diethyl ether were used as fuels in the conditions of the experiments described in Part XIX (6), the thermal efficiency failed to change as it would if expansion ratio were the sole governing factor. The failure is attributed, according to the nuclear theory, to the heat absorbed by endothermic reactions which occurred prior to the completion of combustion and therefore prior to expansion because the timing of ignition, whether by spark or compression, was always adjusted to the optimum value.

It appeared that the approximate magnitude of the adverse effect could be demonstrated by a determination of the difference between thermal efficiencies obtained with the detonating fuels acetaldehyde and diethyl ether, and that obtained when using a nondetonating fuel. Methanol was selected accordingly for experiments to be made in conditions similar to those used for the experiments with acetaldehyde and diethyl ether described in Part XIX. The three fuels contain oxygen in the molecule and all are reputed to be unusable alone for a carburetor engine as usually operated.

The characteristics of methanol as a fuel are the opposite to those of diethyl ether. Thus it is stated frequently that the ether will detonate but not preignite and that methanol will preignite but not detonate. It is also of significance in respect of nuclear ignition that the alcohol burns with a smokeless blue flame when mixed with air in any proportion, whereas only weak mixtures of acetaldehyde or ether with air burn similarly and both substances knock violently when used in normal conditions of engine operation. Ethyl alcohol, 95% ethanol, would have served equally well. There is, however, a great deal

information available concerning that substance when used as the sole fuel for an engine but extremely little about methanol. Ricardo (8, p. 144), in the course of experiments for the Empire Fuels Committee, tried methyl alcohol, "purified wood spirit", as a fuel for the *E 35* engine and found that preignition occurred when the highest useful compression ratio (H.U.C.R.) was 5:1. The engine speed was 1500 r.p.m., the jacket coolant 140° F., and the heat input to the mixture equivalent approximately to that added by a water heated induction system. Synthetic methyl alcohol (methanol) was probably not available at the time of the experiments mentioned and although a great deal of work has since been done in respect of substitute fuels, few references have been found to experiments with methanol as the sole fuel for a carburetor engine; those by Wiebe and Porter, for example, were made with mixtures of the substance with water (13). The feature of importance for present purposes is, however, that spark ignition was always used and that a limitation of heat load was required to prevent preignition.

ARRANGEMENTS MADE TO PROVIDE THE CONDITIONS OF EXPERIMENT

The experiments with methanol were made with a C.F.R. *F. 2.* engine and the auxiliary equipment was as described at some length in Part XIX. The air entering the carburetor was maintained at 50° F., the cooling water entered the cylinder jacket at 95° F. and left the cylinder head jacket at 103° F. The carburetor, as before, was fitted with a $\frac{1}{4}$ in. diameter choke tube which reduced the charge density to approximately 65% of normal with an engine speed of 400 r.p.m. The lubricating oil, S.A.E. 10, in the crank case, was maintained at 120° F.

Technical grade methanol, reputed to be better than 99% pure, was used for the experiments. The boiling point was found not to differ appreciably from that of the pure substance, namely, 64.7° C. (148.3° F.).

A collection is given below of data relative to the three fuels used in this Part to demonstrate the apparent effect of endothermic reactions on thermal efficiency.

TABLE I
DATA IN RESPECT OF METHANOL, ACETALDEHYDE AND DIETHYL ETHER

	Methanol, CH ₃ OH	Acetaldehyde, CH ₃ CHO	Diethyl ether, (C ₂ H ₅) ₂ O
Boiling point	64.6° C., 147° F.	21° C., 69.8° F.	34.6° C., 94.4° F.
Correct A/F, by weight	6.47:1	7.84:1	11.27:1
Lower calorific value, B.T.U./lb.	9100	10550	14567
B.T.U./cu. ft., correct mixture at N.T.P.	96.7	103.0	108.5
Heat of vaporization, B.T.U./lb.	475	245	151
"E", energy of activation, gm. cal./gm. mol.	68000	46000	67000
"E", B.T.U./lb.	3820	1880	1630
Lower limit of inflammability % vapor in mixture with air	6.7	4.0	1.85

The values of "E" given in Table I are those determined by Stavely and Hinshelwood at subatmospheric pressures by the bulb method (10, p. 1568). In order to provide a basis for discussion they may be regarded as relative values in respect of the initiation of decomposition as it occurs in an engine.

The values given in Table I for lower limits of inflammability are for mixtures ignited by spark in closed vessels as given by Coward and Jones (2)

EXPERIMENTAL RESULTS. METHANOL

When describing and discussing experimental results, the term "compression ratio" will be abbreviated to the initial letters C.R. and diethyl ether described as ether.

Spark ignition was always necessary for the experiments with methanol. Timing was fixed at 10° advance, as for the experiments with acetaldehyde and ether, and C.R. was always adjusted to an optimum value as mixture strength was varied. Spark ignition was fully effective solely for mixtures richer than 30% weak. The engine would run on somewhat weaker mixtures

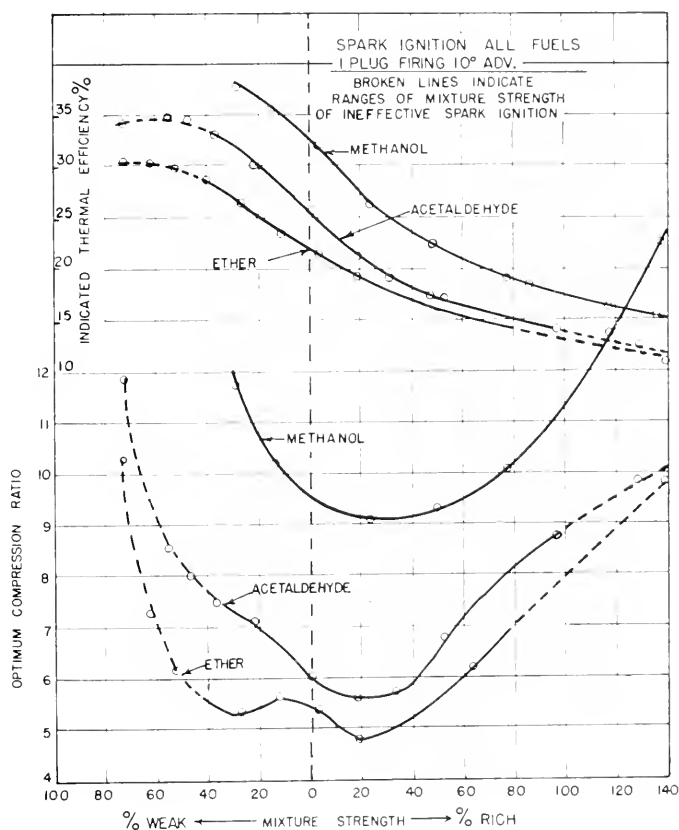


FIG. 1. Optimum compression ratio, thermal efficiency, and related mixture strength. Solid lines indicate spark ignition, broken lines compression ignition.

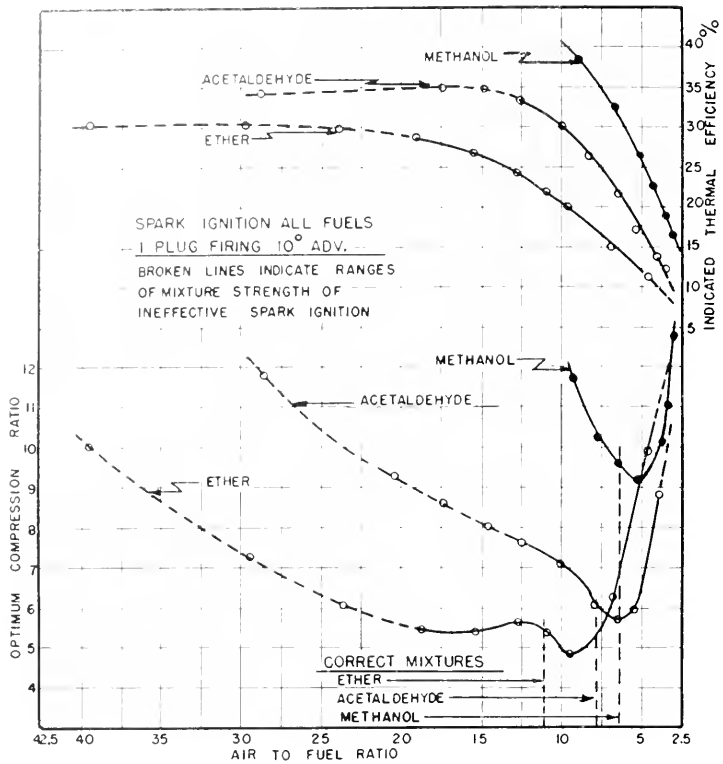


FIG. 2. Optimum compression ratio, thermal efficiency, and related air to fuel ratio. Solid lines indicate spark ignition, broken lines compression ignition.

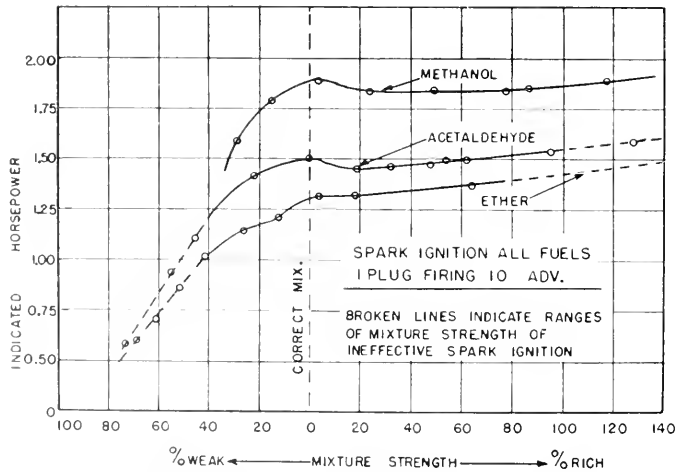


FIG. 3. Relation between power and mixture strength with conditions as used in Figs. 1 and 2.

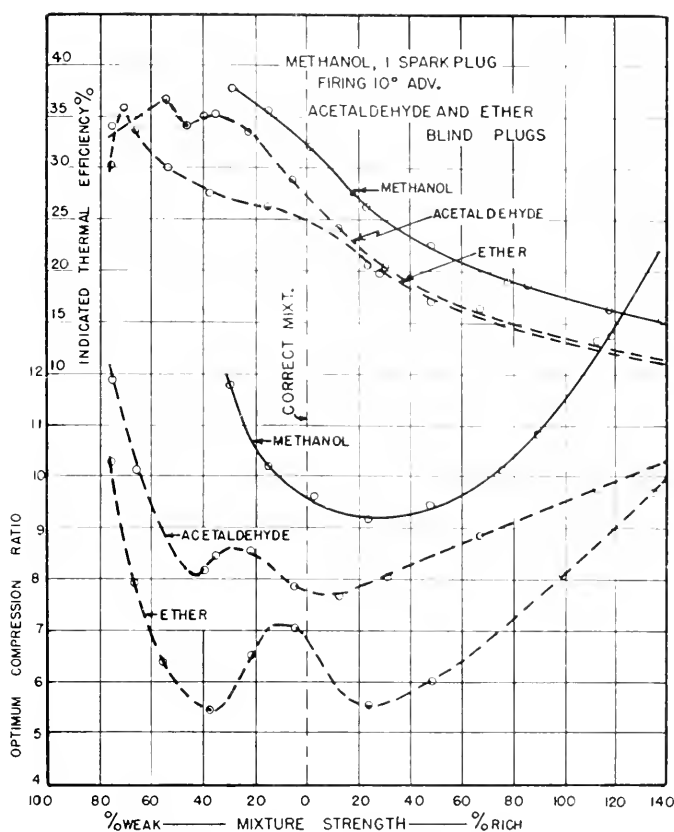


FIG. 4. Optimum compression ratio, thermal efficiency, and related mixture strength; spark ignition for methanol, compression ignition for acetaldehyde and ether.

but ignition became irregular and power diminished rapidly. Attempts to run the engine with ignition by compression always failed although occasional violent explosions occurred when C.R. was increased to 18:1 with a correct mixture or to 25:1 with a mixture 30% weak.

At optimum C.R. combustion was just audible over the mixture range to 100% rich and silent with richer mixtures.

The graphs illustrating the combustion characteristics of methanol are presently given together with similar ones for acetaldehyde and ether as reproduced from Part XIX (6). Experimental results obtained with spark ignition are shown by solid line graphs and those with compression ignition by broken line graphs, in an endeavor to avoid confusion. Two sets of graphs are presented.

The experimental results for methanol are shown by both sets in order to facilitate comparisons. One set, Figs. 1 to 3, shows, in addition, the results of the experiments of Part XIX with acetaldehyde and ether obtained when

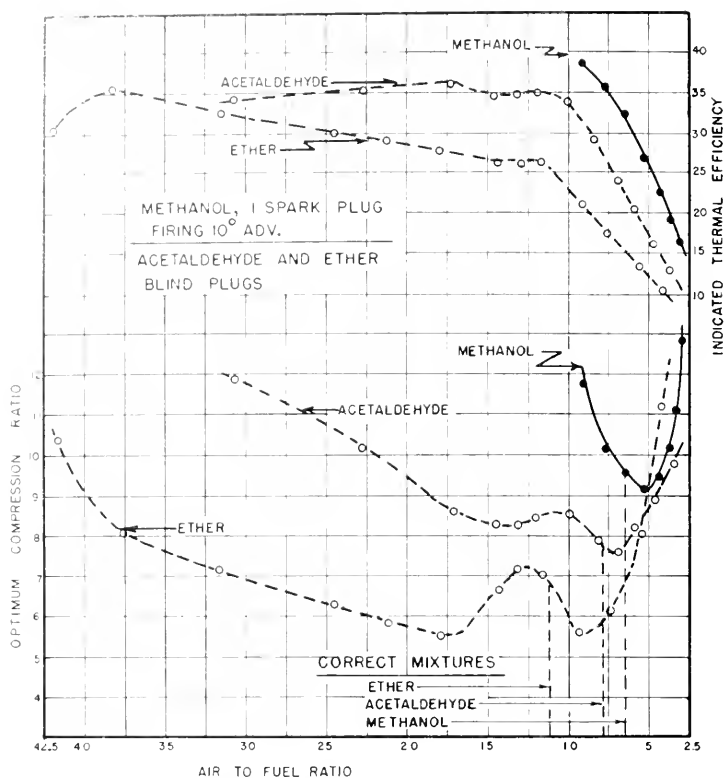


FIG. 5. Optimum compression ratio, thermal efficiency, and related air to fuel ratio; spark ignition for methanol, compression ignition for acetaldehyde and ether.

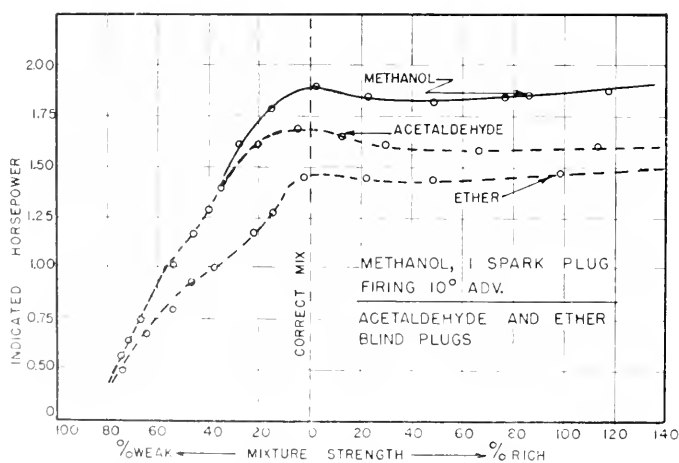


FIG. 6. Relation between power and mixture strength with conditions as used for Figs. 4 and 5.

a single spark plug was used; the spark being effective over that part of the mixture strength range indicated by the solid lines of the graphs. The other set, Figs. 4 to 6, also shows comparable results of experiments with the three fuels but when blind plugs only were fitted to the engine for the experiments with acetaldehyde and ether.

The graphs of Fig. 2 of the first set and those of Fig. 5 of the second set are plotted on a base of air to fuel ratio by weight. This commonly used method of plotting extends the graphs on the weak side of the correct mixture and foreshortens them on the rich side. The method of plotting is therefore useful in displaying the characteristics of the ignition and combustion of weak mixtures although a single datum line for correct mixture cannot be set out for the three fuels concerned.

The volumetric efficiency at the constant engine speed of the experiments and with the fixed diameter carburetor choke tube would normally be affected by the varying heats of vaporization of the fuels used. It should, on this basis, be a maximum with methanol and a minimum with ether, see Table I. The vessel containing the air cooling coils was, however, interposed between the air metering orifice and the carburetor and the consequent restriction of the air supply to the engine varied according to the extent to which the air passageways in it were blocked by frost. This in turn varied with atmospheric humidity. The cooling coils were always defrosted on completing a "run" which, however, including the warming up period, generally required about eight hours. It was not practicable to interrupt a run in order to defrost. The consequent variation of the restriction due to frost was sufficient to mask the change of volumetric efficiency due to differing heats of vaporization. The effect on volumetric efficiency of vaporization in the cylinder was further masked by that which occurred when the wet moisture formed in the carburetor was discharged through the curved choke tube directly onto the inlet valve (see Fig. 5, Part XIX). The factors mentioned above were taken into account by measurement of the rate of air aspirated by the engine and on this basis, the total variation of volumetric efficiency was 5% at correct mixture strength and the maximum value was not always obtained when using methanol as the fuel. The variation is not significant in respect of indicated thermal efficiency. The average volumetric efficiency was 65% of the normal value regarded as being that obtained when the standard C.F.R. carburetor is used.

The power developed when using the three fuels in the conditions of the experiments, Figs. 3 and 6, attained a distinct maximum corresponding to the *correct* mixture when the acetaldehyde or ether was ignited by compression, Fig. 6. The maximum values were less distinctly marked when the substances were ignited by spark as shown by the graphs of Fig. 3. The tendency of indicated horsepower to rise or to remain nearly constant as mixture strength exceeded 30% rich is attributed to the C.R. being raised accordingly and always to an optimum value. The existence of a maximum I.H.P. at correct mixture strength is also attributed to the optimum C.R. having been used.

Indicated horsepower as given by the graphs of Figs. 3 and 6 can be converted to I.M.E.P. by using the factor 53.0. Thus at correct mixture strength the I.M.E.P. when using methanol was 102 lb. per sq. in. The values for acetaldehyde and ether were 89.5 and 77.5 respectively when ignition was by compression, Fig. 6. They were 79.5 and 70.5 respectively with spark ignition, at the necessarily lower values of optimum C.R., Fig. 3.

DISCUSSION

The Lower Limit of Inflammability, Spark Ignition

The lower limits given in Table I for methanol, acetaldehyde, and ether are for percentage concentration of vapor in a mixture with air. They were determined at atmospheric pressure with ignition by spark, in closed vessels. It is of interest to compare them with the values obtained with spark ignition when the mixtures were used in an engine at relatively high temperatures and pressures. The lower limit for acetaldehyde or ether was then attained when mixtures with air became leaner than approximately 40% weak. The exact limiting value was difficult to determine because of the overlapping of spark and compression ignition. When methanol was used as the engine fuel, ignition by spark became irregular when the mixture was leaner than 30% weak and ignition did not occur by compression. The engine continued to run unsteadily on mixtures somewhat leaner than this but power diminished rapidly even on increasing the C.R., probably because, after missing began, the clearance volume could have contained either unburned mixture or products of combustion. Comparable values of lower limits are tabulated below.

TABLE II
LOWER LIMITS (L.L.) OF INFLAMMABILITY OF MIXTURES WITH AIR,
OF METHANOL, ACETALDEHYDE, AND ETHER, WITH SPARK IGNITION

	CH ₃ OH	CH ₃ CHO	(C ₂ H ₅) ₂ O
L.L. (Table I) % concentration in air	6.7	4.0	1.85
L.L. (engine) % in mixture supplied	12.0	4.8	2.03
L.L. (engine) % in ignited mixture taking residual gas as air	9.0	4.2	1.72
Compression ratio at ignition	11.7	7.5	5.5

When correcting for the volume of residual gas added to the aspirated mixture before spark ignition, compression ratio only was taken into account. Thus no allowance was made for the difference in temperature and pressure between it and the mixture as admitted nor for the gas being, in part, products of combustion. These corrections if they could be made would extend the lower limit of inflammability to the least extent for methanol, ignited at a C.R. of 11.7 and to the greatest extent for ether, ignited at a C.R. of 5.5. Thus the corrections would extend the lower limit for ether to a value less than 1.72 which even without the corrections is less than the value of 1.85 given in Table I. The relatively high temperatures and pressures in the engine appear therefore to cause the greater increase in inflammability with the detonating fuels.

Ideal Efficiency Compared with the Value Observed with Methanol as a Fuel

Values for ideal efficiencies of real engines as given in works of reference are calculated as being those attainable when the working fluid contains products of combustion of the fuel and depend accordingly on expansion or compression ratio if the two are equal and on the concentration of fuel in the mixture with air. The effect of fuel concentration on efficiency depends then on the specific heats of the products of combustion, taken over the temperature range of expansion and the dissociation which may occur at temperatures of combustion. The value of " n " in the expression $\left(\frac{1}{r}\right)^n$ is reduced accordingly as the concentration of fuel increases, with the consequence that thermal efficiency, as given by the expression $1 - \left(\frac{1}{r}\right)^n$, diminishes.

Computations of ideal efficiencies present many difficulties but were made by Tizard and Pye (12, p. 13) for mixtures of air with benzene, with compression ratios* rising from 4 to 10 and based on values of specific heats available at the time. A partial revision was made by Pye (7, p. 181) when more accurate data for specific heats at high temperatures became available. The probable typographical error in the equation given for efficiency should be noted. The graphs obtained accordingly for the relations between efficiency and compression ratio for three mixture strengths have been extended to a compression ratio of 20 and by interpolation to include graphs for mixtures 75% weak and 10% rich (see Fig. 7). The extension to a C.R. of 20 is necessary because the C.R. used for experiments of the present series frequently approaches that value. Graphs for additional mixture strengths are necessary in order to obtain a sufficient number of points on a single graph when both C.R. and mixture strength are variables.

The ideal efficiencies given by the graphs of Fig. 7 are based on the thermodynamic properties of the combustion products of a hydrocarbon and may not be strictly applicable to the results of experiments with methanol as the fuel for an engine. It may safely be assumed, however, that graphs for ideal efficiencies when methanol is used, and calculated similarly, would merely be displaced to some extent from those for benzene, Fig. 7, the form being unaltered.

A comparison is given accordingly by the graphs of Fig. 8, of ideal efficiencies, with those observed when methanol was used as the fuel for the C.F.R. engine. Methanol is a nondetonating fuel because, according to the nuclear theory, it cannot be decomposed in the engine to the extent necessary for the formation of nuclei of ignition. Spark ignition is therefore always necessary and the graph for observed efficiencies is of the same general form as that for ideal values but not parallel to it. Thus it will be noted that the departure of observed from ideal efficiency increases with increase of compression ratio, as would be expected because of the extent of decomposition increasing accord-

* Compression and expansion ratios have equal numerical values in piston engines as generally constructed.

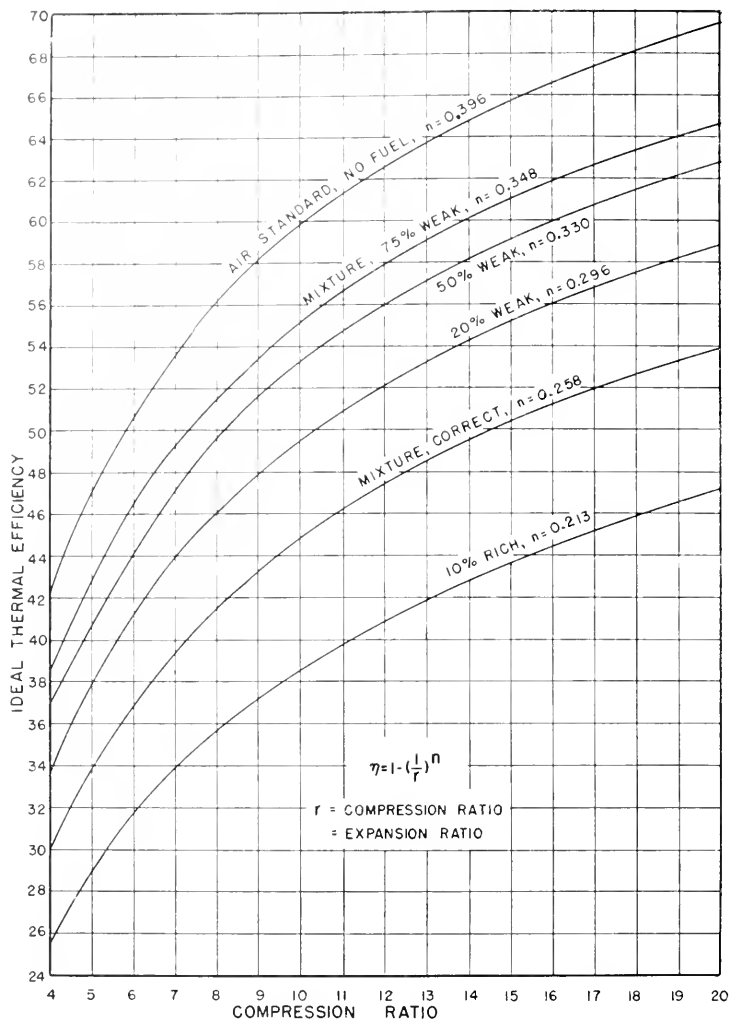
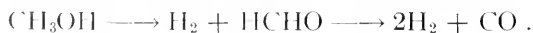


FIG. 7. Relation between ideal efficiency and compression ratio as affected by mixture strength, according to ordinary rules of calculation.

ingly. Methanol is known to decompose in stages and according to Fletcher (4),



An endothermic reaction is therefore possible in the engine and the first stage would yield volumes of hydrogen and formaldehyde each equal to the volume of the methanol vapor before decomposition; the second stage provides two volumes of hydrogen and one of carbon monoxide. Formaldehyde is not a proknock according to recent experiments by Downs, Walsh, and Wheeler (3, p. 180) and carbon monoxide cannot be dissociated at engine temperatures to yield the carbon required for nuclear ignition. The hydrogen formed profusely even by the first stage of decomposition may safely be assumed to

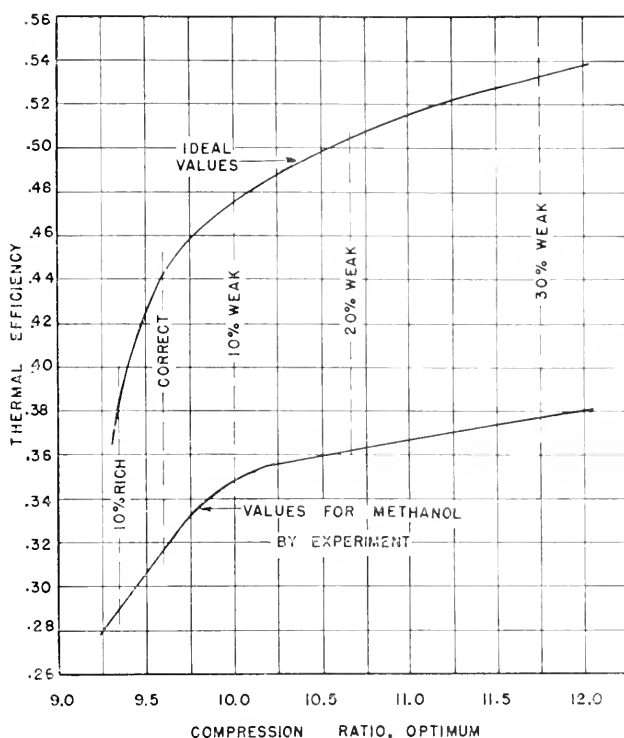


FIG. 8. Values of ideal efficiency from Fig. 7, compared with values observed when using methanol.

account for the preignition which limits the C.R. at which methanol can be used in the ordinary temperature conditions of engine operation.

Comparable Thermal Efficiencies. Methanol, Acetaldehyde, and Ether

It is shown by the graphs of Fig. 8, for experiments with methanol, a non-detonating fuel, that thermal efficiency *tends* to vary with C.R. and mixture strength in accordance with the ordinary rules of calculation which take into account postcombustion effects only. The lack of complete accord is attributed to some degree of decomposition occurring prior to the completion of combustion with a consequent irrecoverable loss of heat. A greater lack of accord would be expected when using detonating fuels, according to the nuclear theory of ignition, because of the necessarily greater degree of decomposition. The expectation is confirmed by the experimental results exhibited by the graphs of Figs. 9 to 12 for the efficiencies observed when using acetaldehyde and ether as compared with that observed when using the nondetonating methanol.

Thermal efficiencies given by the graphs are indicated values taken from Figs. 1 and 4, but instead of being plotted against mixture strength are, as for Fig. 8, plotted against optimum compression ratio with values increasing as

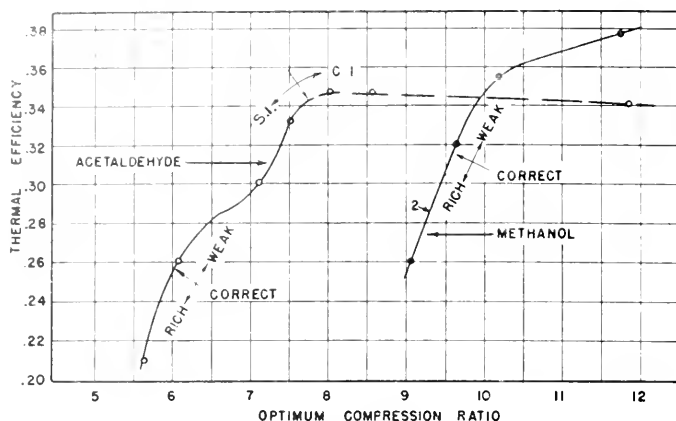


FIG. 9. Methanol and acetaldehyde. Observed relation between thermal efficiency and optimum compression ratio; methanol ignited by spark, acetaldehyde ignited by spark over range of mixture strength indicated by solid line part of graph and by compression as shown by broken line part.

mixture strength decreases. Spark ignition is indicated as having been used when the graphs are solid lines. Broken lines indicate ignition by compression and the changeover from spark to compression ignition obtained when using aldehyde or ether at lower compression ratios than required for compression ignition is also marked on the graphs by arrows pointing to compression ignition, C.I., or to spark ignition, S.I. Especially noteworthy features exhibited by the graphs are as follows:

(1) The great *deviation* of the detonating fuels acetaldehyde and ether as compared with that of the nondetonating fuel methanol, from the ideal relation between thermal efficiency and compression ratio, as calculated by

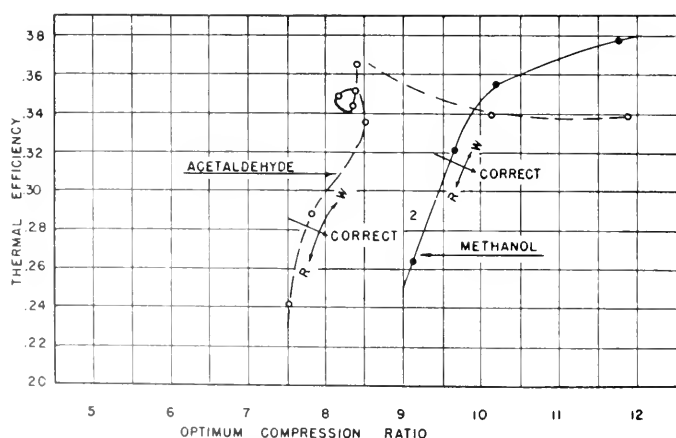


FIG. 10. Methanol and acetaldehyde. Observed relation between thermal efficiency and optimum compression ratio, acetaldehyde ignited by compression, methanol by spark.

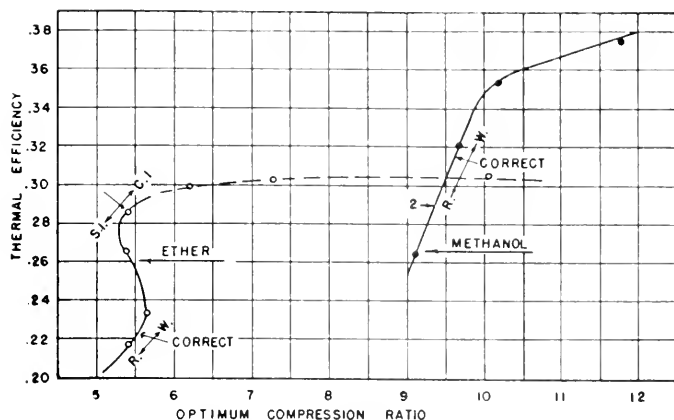


FIG. 11. Methanol and ether. Observed relation between thermal efficiency and optimum compression ratio; methanol ignited by spark, ether by spark over range of mixture strength indicated by solid line part of graph and by compression as shown by broken line.

taking into account effects occurring only after completion of combustion. The deviation is greater for ether than for acetaldehyde which detonates less readily.

(2) The graphs, especially those for acetaldehyde and ether, indicate two phases of ignition. The indication is more pronounced for ether than for acetaldehyde. It is also the more pronounced at the higher compression ratios used to obtain compression ignition over the mixture range 40% weak to 80% rich. Thus the loops shown by the graphs of Figs. 10 and 12 are believed to be coincident with the change from one phase of ignition to another. The changeover, Figs. 9 and 11, is marked by the pronounced in-

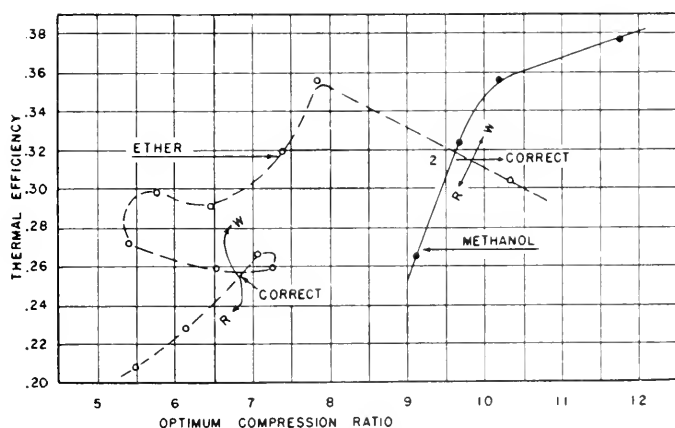


FIG. 12. Methanol and ether. Observed relation between thermal efficiency and optimum compression ratio, ether ignited by compression, methanol by spark.

which occurs when spark ignition ceases to be effective and is succeeded by compression ignition.

3. The thermal efficiencies observed with compression ignition when a spark plug is in place but not fired, differ in magnitude and pattern from those obtained with compression ignition when all plugs are mild steel blanks. The difference is more pronounced for ether than for acetaldehyde (compare second phases of ignition, Figs. 9 and 10 for acetaldehyde with Figs. 11 and 12 for ether).

The Nuclear Theory of Ignition and Endothermic Decomposition Reactions

It is essential to the nuclear theory as stated in Part IV (6) that fuels subject to detonation in an engine decompose to provide material nuclei on which oxidation reactions can occur *in* an air-fuel mixture. That is, decomposition must precede oxidation. Decomposition of the fuels in an engine is an endothermic reaction and the validity of the nuclear theory is believed to be confirmed by the occurrence in engine experiments of a corresponding loss of thermal efficiency.

A fuel molecule has a definite probability of decomposing to others of lower molecular weight if it acquires energy equal to or greater than the "energy of activation", which is given in terms of gram-calories per gram-mole and designated by the symbol " E ". The temperature at which decomposition begins depends on the stability of the molecule and the value of E diminishes with increase of pressure. The percentage decomposition increases with time of exposure to the temperature and pressure conditions for which E has a particular value. That is, a continuous absorption of heat is required to maintain the decomposition reaction. If it be carried out at the temperature required for its initiation, the products are in large part unsaturateds containing fewer carbons in the molecule than were contained in that of the parent substance. The velocity of the reaction increases rapidly with increase of temperature above that required for its initiation. Unsaturateds are then formed at a decreasing rate; carbon, lower saturateds, and hydrogen at an increasing rate.

E , for a particular substance, has a maximum value when the decomposition reaction is homogeneous. Lower values are obtained if the surface of the reactor in which decomposition occurs is such that the reaction becomes in part heterogeneous. Values of E given in works of reference have usually been determined in quartz reactors at subatmospheric pressures and are reputed to be for homogeneous reactions. They cannot be applied quantitatively to decomposition reactions which occur at the relatively high pressures in the combustion chamber of an engine which contains various metal surfaces heated unequally when power is being developed. The values of E , Table I, may however be used to indicate the relative tendencies of methanol, acetaldehyde, and ether to decompose in an engine. The relative weights of the substances in correct mixtures with air are the reciprocals of the air-fuel ratios given in Table I and if multiplied by the respective B.T.U. values per pound

required to initiate decomposition give relative values for the heat required for decomposition in the engine as below:

Methanol	592
Acetaldehyde	212
Ether	145

According to the nuclear theory, the relative values may be taken to represent the antiknock properties of the fuels and are in agreement with experimental results, remembering that methanol decomposes to yield hydrogen in a concentration sufficient to account for preignition in a hot engine and that this occurs prior to the formation of nuclei.

Nuclear Ignition as Promoted by Pressure Waves

The decomposition by a single application of pressure of the whole of the fuel in a mixture with air in an engine, to the extent required to produce a uniform igniting concentration of nuclei throughout the mass, would require a relatively large quantity of heat and the resulting detonation would probably be disastrous. In practice either in engines or in compression ignition machines, temperature in the combustible mixture is not uniform on completion of compression. In an engine using liquid fuels, mixture strength also is not uniform. Thus decomposition can occur preferentially in one or more small parts of the compressed mixture and provide therein the concentration of nuclei required for autoignition. One or more pressure waves could then be generated which on passing through a mixture already heated by compression would raise it progressively to the higher temperature required for decomposition and consequent nuclear ignition. The rate of flame propagation in the major portion of the combustible mixture would then be the resultant of the pressure wave velocities. Thus it appears to be possible to create pressure waves which will detonate the mixture in the combustion chamber of an engine without the preliminary length of flame "run" which is otherwise necessary.

The creation of a pressure wave in the *end gas* is discussed by Serruys (9). He postulates that at one place or another the end gas will have a point at a maximum temperature and that a small globular region around the point will have a uniform temperature and pressure which will increase as the flame front advances until autoignition occurs and starts a pressure wave which will pass through and ignite the remainder. It is further suggested that the temperature level in the globule may be such that the majority of hydrocarbons are cracked before self-ignition occurs and that the newly formed molecules will the more readily combine with oxygen. Serruys appears to envisage the formation of nuclei of gaseous globules and applies his hypothesis solely to the part of the charge remaining unburned after flame has been initiated by a spark. Nevertheless, the hypothesis of Serruys in respect of the creation of a pressure wave does not differ in principle from that advanced in this Part. The two differ mainly in respect of the degree of decomposition required to cause ignition.

A pressure wave is not required for the production of the concentration of

on. It is possible that the autoignition of a small quantity of end gas in a spark ignition engine because the necessary temperature and pressure conditions have been obtained correspondingly late in the period of combustion. A pressure wave would be created but would then pass through a mixture in which combustion was far advanced. The sole effect would be to hasten the process. An explanation is obtained accordingly for the appearance of flame in the whole of the mixture nearly simultaneously with detonation by the end gas. If, however, the end gas were of relatively large volume or if the whole of the charge were to be ignited by compression, the function of the pressure wave would be to produce nuclei of ignition as it passed through a combustible mixture which had not been raised to the necessary extent by compression to the pressure and temperature required for decomposition of the fuel to an advanced stage.

Decomposition by a pressure wave of a hydrocarbon fuel in a compressed mixture with air, to the extent necessary to release copious quantities of free carbon, was mentioned by Miller in the discussion of the paper on ignition by compression by Taylor and others (11, p. 273) as having been demonstrated by himself and his associates, with the aid of high speed photography. This work together with the experimental results for compression ignition described in the paper which Miller discussed is of especial interest in respect of further experiments on the causes of ignition of hydrocarbon fuels which will be described in subsequent Parts.

ACKNOWLEDGMENTS

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**THE OXIDATION, DECOMPOSITION, IGNITION, AND
DETONATION OF FUEL VAPORS AND GASES**

**XXI. NUCLEAR IGNITION AS ILLUSTRATED BY THE CHARACTER-
ISTICS OF COMPRESSION AND SPARK IGNITION; PENTANE,
HEXANE, AND HEPTANE AS ENGINE FUELS**

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XXI. NUCLEAR IGNITION AS ILLUSTRATED BY THE CHARACTER- ISTICS OF COMPRESSION AND SPARK IGNITION; PENTANE, HEXANE, AND HEPTANE AS ENGINE FUELS¹

BY R. O. KING², E. J. DURAND³, A. B. ALLAN⁴,
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ABSTRACT

Experiments made with acetaldehyde and diethyl ether as fuels for the C.F.R. carburetor type engine, described in Parts XIX and XX, supported the view that autoignition of the end gas as indicated by knocking combustion, was due to a decomposition reaction in the fuel which provided nuclei of ignition. The compression ratio, in the special conditions of the experiments, could be raised to obtain autoignition before t.d.c. The engine could then be run without spark ignition. The timing of autoignition could be varied as required to obtain maximum values of power and thermal efficiency at any particular mixture strength, by adjustment of compression ratio to a corresponding optimum value. The essential features of the special conditions were a subnormal charge density, required to prevent unduly severe combustion knock as mixture strength approached and then exceeded the correct value and relatively low surface temperatures in the combustion chamber as required to prevent the formation of products of surface oxidation at an appreciable rate. The engine then became a compression ignition machine which differed from the conventional single stroke variety in having an exhaust valve and also in the fact that ignition delay occurred necessarily during compression instead of being reckoned as beginning on its completion. It is therefore of interest that characteristics of ignition by compression as determined by the engine experiments of this Part are in agreement with those determined by experiments with the M.I.T. single stroke rapid compression machine, in so far as comparable experiments have been carried out. Experiments made in the "special" conditions and with nearly normal varieties of heptane, hexane, and pentane are described in this Part. Compression ratio was always adjusted to the value for which power output was a maximum. This value is described as the optimum compression ratio (Opt. C.R.). The method of determination of Opt. C.R. and the variation with mixture strength, when ignition is by compression, is described in some detail in the text and illustrated by numerous graphs. The graphs for the relation between Opt. C.R. and mixture strength were always of the W form similar to those given in Part XIX for acetaldehyde and diethyl ether, obtained in like special conditions. The graphs indicate, as explained in Part XX, that the departure of thermal efficiencies from ideal values may be attributed in part to the adverse effect of the endothermic decomposition reaction required to provide nuclei of ignition during the compression stroke. Pressure-time indicator diagrams for an extremely weak heptane-air mixture are given. They show that maximum combustion pressure occurs at 10° after t.d.c. when compression ratio is adjusted for maximum power output, that is to the optimum value. Also that maximum combustion pressure timing advances as compression ratio is raised beyond the optimum value until it occurs before t.d.c. and power output becomes zero. The preignition thus obtained with compression ignition is described as nuclear preignition. The pressure-time diagrams show two stages of combustion

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very clearly. The first stage is regarded as including the delay period in part. The two stages are shown in a striking manner by a dp/dt diagram. A pressure-time diagram taken at nearly correct mixture shows that maximum combustion pressure at Opt. C.R. occurs as before at 10° after t.d.c. but that combustion is a single stage effect with pressure rising extremely rapidly. The experimental results mentioned above were all obtained with blank steel plugs in place of the spark plugs and bouncing pin. It was found however, on replacing one of the blank plugs with an unfired spark plug, that optimum compression ratios corresponding to mixtures richer than approximately 30% weak were substantially reduced. The igniting effect remained after removal of the electrodes. It could not be due to direct surface ignition in the low temperature conditions of the experiments and is attributed to the initiation of a pressure wave by the preferential decomposition and consequent nuclear ignition of the mixture adjacent to the spark plug core which is probably the surface of maximum temperature in the combustion chamber. It was found earlier that spark ignition at 10° in advance of t.d.c. became ineffective for mixtures leaner than approximately 40% weak. A similar spark ignition failure was shown by experiments of this Part made with spark timing varied from 20° to 5° advance. Compression ratio was always adjusted to the optimum value in order that maximum combustion pressure would occur at 10° after t.d.c. The Opt. C.R. attained relatively high values as spark ignition was retarded and the graphs relating it to mixture strength tended to assume the W form obtained with ignition by compression indicating that at relatively high values of Opt. C.R. impregnation of the mixtures by products of fuel decomposition was sufficient to increase rate of flame propagation but not to cause autoignition. As spark ignition became ineffective it was succeeded by compression ignition provided compression ratio were always raised to at least the optimum value as mixture strength was reduced. Special experiments for which power was supplied to maintain speed when B.H.P. became less than zero demonstrated that ignition by compression occurred even when the mixture was leaner than 93% weak, that is when the air-fuel ratio by weight was greater than 220:1. Systematic examinations of the deposits remaining on surfaces in the combustion chamber were made in the course of the compression ignition experiments described in this Part. The first indication of a deposit was a brown color found on the cooler surfaces after the briefest possible time of running. It could be wiped off easily and it is of interest that a similar color was found on surfaces in the combustion space of the M.I.T. machine after an ignition by compression of a hydrocarbon fuel. The color was therefore not due to decomposition of lubricating oil. In the engine, the color became a definite deposit of a granular nature after some hours of running on a weak mixture and appeared to be of a resinous nature which indicated condensation products of aldehyde. Some carbon was however generally present. Finely divided carbon appeared as the sole deposit as mixture strength was increased until at correct mixture the carbon deposit covered a large part of the combustion chamber surface. At richer mixtures the carbon formed a layer over the entire surface and black smoke appeared in the exhaust. The ignition characteristics exhibited by the experiments described in this Part and earlier in Part XIX are obtainable solely in conditions of low heat load which ensures that decomposition and oxidation reactions occur mainly if not entirely in the gaseous phase. Thus it is shown by the final experiments of this Part that when heat load is increased by raising the jacket coolant and mixture temperatures to the values used for the motor method of knock rating, other conditions of the method of experiment remaining unchanged, the relation between Opt. C.R. and mixture strength tends to be represented by a single graph regardless of whether ignition is by compression with or without an unfired spark plug or by spark at 10° in advance of t.d.c. and a transition occurs from the W to the familiar U form of graph.

INTRODUCTION

Experiments described in Part XVII (4) demonstrated that a standard C.F.R. knock testing engine could be run without spark ignition over a wide range of pentane-air mixtures if compression ratio were always adjusted to maintain a particular standard of knock intensity as indicated by the bouncing pin meter. Volumetric efficiency and consequent charge density were higher than usual because the shrouded inlet valve had been replaced with one of the common type,

The engine was run at the low speed of 400 r.p.m. and the air supply and jacket coolant maintained at unusually low temperatures. Exceptionally high values were obtained for thermal efficiency although compression ratio could not be increased sufficiently, when using other than weak mixtures to obtain a value corresponding to maximum power output, because of the incidence of a knock intensity greater than that adopted as standard.

It seemed remarkable at the time that a carburetor type engine in exceptionally cool conditions of operation would run without spark ignition because that effect in practice generally occurs when an engine is hot and is then attributed to preignition arising from a surface in the combustion chamber, such as a spark plug or an exhaust valve, having become overheated. It was concluded from a consideration of the characteristics of performance of the engine that ignition had been by compression and a consequence of the decomposition of the fuel to provide nuclear centers of ignition in the combustible mixture.

The method of experiment was next used for a determination of the combustion characteristics of acetaldehyde and diethyl ether although both substances knock violently when used as engine fuels in normal operating conditions. The experiments are described in Part XVIII (5). The results demonstrated that the combustion characteristics, in the low engine temperature conditions, were broadly similar to those previously obtained when using pentane. Thus although compression ratio could be adjusted until the engine would run without spark ignition, it could not be increased further to obtain maximum power output unless the knock intensity adopted as standard were exceeded. Moreover, the audibility of knocking combustion did not always correspond with the intensity indicated by the knock meter. Furthermore, in view of the ease of vaporization by ether and acetaldehyde it appeared that the presence of liquid drops in the fuel-air mixture was not essential to the decomposition of the fuel to the extent necessary for the provision of nuclear centers of ignition.

Subsequent to the experiments mentioned above it was found that if charge density were below normal, compression ratio could be raised and adjusted to the value required for maximum power output without giving rise to an excessive intensity of knocking combustion even when using correct mixtures with air of either acetaldehyde or diethyl ether. This procedure made possible a determination of the relation between compression ratio and maximum power output for any value of mixture strength. Experimental results obtained accordingly were more easily repeatable and more significant than those obtained by adjusting compression ratio for a standard knock intensity as indicated either by the bouncing pin or by the level of audibility.

Refrigeration equipment for the air supply to the carburetor was provided at this stage of the investigation, and it was no longer necessary to rely upon uncertain winter weather for a supply of dry cold air. Thus the conditions required for what had developed into a new method of experiment could be standardized in order that comparable results might be obtained for experiments with various fuels when ignition was either by spark or compression.

The conditions adopted as standard, and the arrangements made to provide them, are described in some detail in Part XIX (6). Those of prime importance are stated here as a convenience and are: (1) a subnormal charge density; (2) an engine speed of 400 r.p.m.; (3) jacket coolant at 95°F. inlet, 100°F. outlet; (4) air supply to carburetor 50°F.; (5) spark ignition when used, 10° in advance of arrival of the piston at top dead center (t.d.c.); and (6) compression ratio always adjusted to obtain maximum power output, that is, to an optimum value.

The new method of experiment was used for the experiments with acetaldehyde and diethyl ether described in Part XIX (6) and for those with methanol, for which spark ignition was necessary, described in Part XX (3). The experimental results appeared to be of considerable interest in respect of the nuclear theory of ignition and the fundamentals of detonation but because of recent publication they need not be discussed here. It should be mentioned, however, that the carburetor type engine seemed to have become a compression ignition machine comparable in many respects with the single stroke variety while possessing the advantage that characteristics of compression ignition could be related to engine performance in terms of power and thermal efficiency. It was decided, therefore, to use the new method of experiment for a further investigation of the combustion characteristics of *n*-pentane and in addition for a determination of those of hexane and heptane.

Normal paraffins as supplied by Phillips Petroleum Company were used for the experiments. The pentane and hexane were technical grades. The heptane was the nearly normal grade approved by the A.S.T.M. as a reference fuel for knock rating. Relevant data are tabulated below.

The lower calorific values of Table I were used for calculating thermal efficiencies.

TABLE I
DATA IN RESPECT OF THE PARAFFIN FUELS

	Pentane	Hexane	Heptane
Boiling point, normal variety, °F.	96.9	155.7	209.2
Heat of vaporization, B.T.U./lb. at b.p.	153.6	144.8	137.5
Higher calorific value, B.T.U./lb.	20914	20771	20668
Lower calorific value, B.T.U./lb.	19345	19238	19160
Correct A/F ratio, by weight	15.31	15.24	15.18

A C.F.R.-F.2 engine with a swinging field d-c. electric dynamometer was used and differed from standard in being fitted with three spark plugs and an unshrouded inlet valve.

The volumetric efficiency in the standard conditions of the new method of experiment was 85%. The corresponding charge density is described as "normal". Charge densities of 64 and 78% of normal were used in the course of the experiments. If pressure at the beginning of compression were atmospheric, volumetric efficiency at a particular temperature would be 100% and

the charge densities of 64 and 78% at the same temperature would be approximately 54 and 66% of atmospheric density.

The terms compression ratio, optimum compression ratio, and mixture strength are abbreviated in the text to C.R., Opt. C.R., and M.S., respectively.

RESULTS OF EXPERIMENTS

Compression Ignition and the Determination of Optimum Compression Ratio

The method adopted for the determination of optimum compression ratio, when ignition is by *compression*, cannot be used with fuels liable to detonation unless charge density is less than normal, as shown by the experiments with acetaldehyde and diethyl ether described in Part XIX (6). The application of the method to more comprehensive experiments with paraffin fuels requires an elaboration of its earlier description and experiments made with hexane and heptane will suffice for the purpose. The experiments were made with a charge density of 64% of normal after substituting blind plugs of mild steel for the three spark plugs and the bouncing pin.

The engine was started from cold with little or no shock by using a relatively high compression ratio and a weak mixture. This starting method was used for a series of experiments extending over a period of several weeks during which spark ignition was never used. After starting in this way, C.R. was reduced and the engine run for the time required to stabilize temperatures. The rate of fuel consumption and the power output (B.H.P.) were then observed; speed being maintained at 400 r.p.m. by manual control. The operation was repeated as C.R. was varied by steps, in order to obtain values of power output passing through a maximum. The results were then plotted to obtain a graph for the relation between power output and C.R. for the particular value of the M.S. A similar relation between power output and C.R. was then obtained for other values of M.S. and a series of graphs plotted accordingly.

A selection from the series obtained as a result of experiments with hexane is exhibited by Fig. 1, and it will be seen that for any one of the values of M.S. there is a particular C.R. for which power output is a maximum. The broken line graph drawn through the optimum values thus determined is of the W form similar to that given in Part XIX (6) as a result of experiments with acetaldehyde and diethyl ether, but the form is distorted because of the non-linear relation between power and M.S. All of the graphs required to delineate the broken line graph are not shown because of the complexity that would be due to overlapping. A similar set of graphs but plotted on a base of indicated mean effective pressure (I.M.E.P.) is given, Fig. 2, for experiments with heptane.

A comparison of Figs. 1 and 2 shows that, for medium rich mixtures, the graphs relating C.R. and I.M.E.P. (Fig. 2) do not exhibit the well-defined Opt. C.R. shown when C.R. was related to B.H.P., as in the graphs of Fig. 1. The comparison shows also that the knock intensity for rich hexane-air mixtures, as described, is heavier than for similar heptane-air mixtures. The

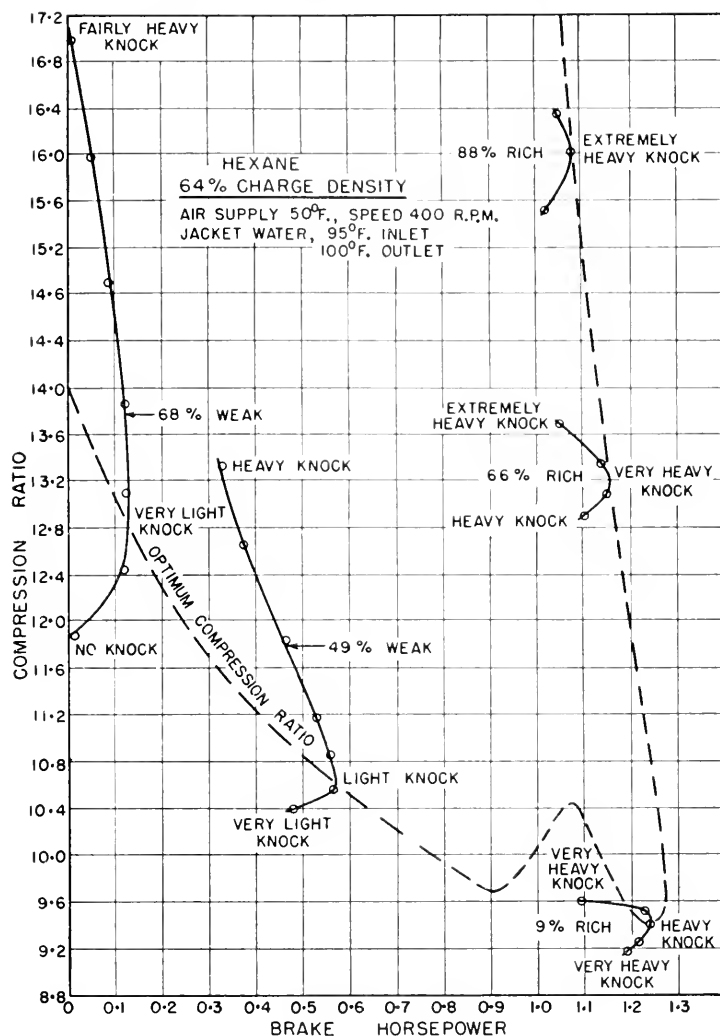


FIG. 1. Results of experiments made to determine optimum compression ignition timing. Hexane-air mixtures.

difference is attributed to the higher compression ratios required for the nuclear ignition of hexane. Thus further experiments described in this Part, see Fig. 6, show that for a hexane-air mixture 80% rich the Opt. C.R. was 16 whereas an Opt. C.R. of 12.5 only was required with a similar concentration of heptane in the mixture with air.

Nuclear Preignition

It has been assumed that ignition by compression is a nuclear effect and Opt. C.R. has been taken as the value for which power output (B.H.P.) was a maximum. The time of the occurrence of maximum combustion pressure, in

degrees of crank angle after t.d.c. must then have been the optimum. The decrease of power output observed as compression ratio is *raised* to beyond the optimum value, when using a particular value of mixture strength, is therefore attributed to the corresponding advance in the time of occurrence of maximum combustion pressure. That time is dependent on the time of nuclear ignition and the length of the delay period, and the decrease of power output is attributed to nuclear preignition. On the other hand, the decrease of power observed as C.R. is *lowered* from the optimum value is attributed to a retardation of the time of occurrence of maximum combustion pressure and the corresponding time of nuclear ignition. Thus, referring to Fig. 2, it will be seen that for heptane-air mixtures, 71, 62, and 53% weak, C.R. could be raised beyond the optimum value until power output became zero, without the occurrence of an intolerable knock intensity.

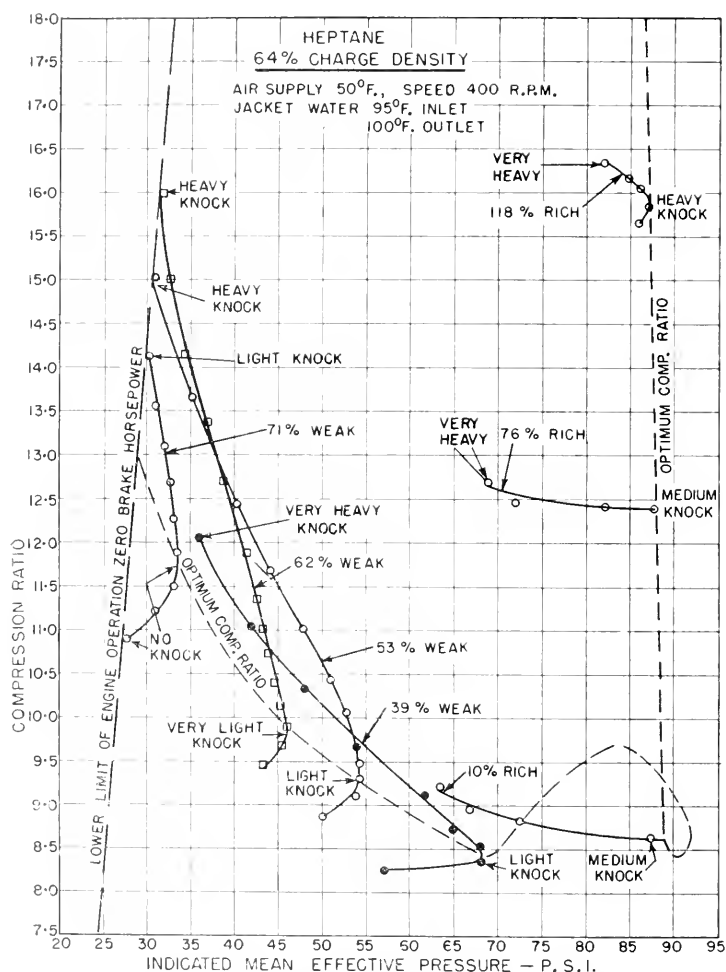


Fig. 2. Results of experiments made to determine optimum compression ignition timing. Heptane air mixtures.

The possible decrease below the optimum value was relatively small. That is, there was a narrow variation of C.R. between the optimum and the value for which ignition did not occur or for which B.H.P. was zero.

Data from Fig. 2, relating to the effect of nuclear preignition obtained on using compression ratios higher than the optimum value, are tabulated below for heptane-air mixtures ranging from 39% weak to 118% rich. These are mixtures for which C.R. could not be raised sufficiently to reduce power output to zero because of the consequent intolerable intensity of knocking combustion.

What is described in the table as "very heavy knock", which was always accompanied by unstable running, may be taken as indicating the maximum permissible degree of nuclear preignition, that is, ignition occurring at a higher than the Opt. C.R. Then, on this basis, the engine will, for example, tolerate a degree of nuclear preignition sufficient to reduce indicated power by 45% when the mixture is 39% weak, by 29% when it is 10% rich, and by 6% only when it is excessively rich.

It is to be remembered that the data of Table II were obtained in the standard conditions of the new method of experiment and when the charge density was 64% of normal.

TABLE II

DECREASE OF POWER WITH INCREASE OF COMPRESSION RATIO TO BE HIGHER THAN THE OPTIMUM VALUE

Mixture strength	C.R. for max. power	C.R. for v. heavy knock	I.M.E.P. decrease	Per cent decrease
39% weak	8.4	12.1	From 68 to 36	47
20% "	9.4	10.7	" 81 to 53	37
10% rich	8.6	9.2	" 89 to 63	29
72% "	12.4	12.7	" 87 to 69	21
118% "	15.8	16.4	" 87 to 82	6

Characteristics of Nuclear Preignition, Two Stage Combustion, and the Delay Period as Shown by Indicator Diagrams

A Sunbury electronic indicator with a variable magnetic flux pressure pickup was used to obtain the diagrams. A notched timing wheel mounted on the outboard end of the dynamometer shaft of the C.F.R.-F.2 unit, provided blips on pressure-time diagrams at 10° intervals. The lack of uniform spacing of the blips as they appear on the diagrams is due to the variable pressure on the engine piston acting on a somewhat flexible transmission to the timing wheel. The blips on the pressure-time diagrams as reproduced have, for the sake of clarity, been indicated by added vertical lines. Long vertical lines indicate blips at t.d.c. and shorter ones, those at 10° intervals for 30° before and after t.d.c.

The diagrams, Figs. 3, 4, and 5, were taken when the engine was running on compression ignition in the standard conditions of the new method of experiment, with charge density 64% of normal. They depict the characteristics of combustion as described below. The term "maximum combustion pressure" will be abbreviated to Max. C.P. because of frequent use.

Referring to diagram No. 1 of Fig. 3, it will be seen that Max. C.P. is at 18° after t.d.c. with a C.R. of approximately 10.

Diagram No. 2 shows that an increase of C.R. to 10.3 caused Max. C.P. to advance 8° , that is, to 10° after t.d.c., and the graph relating C.R. to power shows that I.M.E.P. had increased from 30 to 32.5 p.s.i. which is the maximum attained. The C.R. of 10.3 may therefore be taken as the optimum value.

Diagram No. 3 shows the effects of raising the compression ratio to 10.9. The Max. C.P. increases but as C.R. is then higher than the optimum value, I.M.E.P. decreases from the maximum of 32.5 to 31.0 p.s.i. This effect is due to the advance of Max. C.P. from 10° to 6° after t.d.c. and the consequent beginning of nuclear preignition.

Diagram No. 4 shows the effects of a further increase of C.R. to 12.8. Max. C.P. advances to 4° before t.d.c. and rises to a relatively high value but, as it occurs before t.d.c., I.M.E.P. is reduced to 29 p.s.i. which is the value obtained when B.H.P. is zero. That is, an advance in the time of occurrence of Max. C.P., of from 10° after, to 4° before, t.d.c., has had the effect of reducing power output from the maximum possible value to zero because of the degree of nuclear preignition.

The diagrams of Fig. 3 show two stages of combustion. The first is regarded as the "delay period" and diagram No. 1 shows that it extends from 10° before to 10° after t.d.c. when C.R. is 10.0. Therefore the phenomenon occurs at nearly constant volume but with a pressure rise during the 10° before t.d.c. The time of the occurrence of the delay period advances as C.R. is increased and the length in degrees of crank angle diminishes until, with a C.R. of 12.8 it begins at 13° and ends at 9° before t.d.c. Thus at the engine speed of 400 r.p.m., the time of the delay period diminishes from 8.4×10^{-3} sec. to 1.7×10^{-3} sec. as the C.R. is raised from 10 to 12.8.

It will be seen by further reference to the diagrams of Fig. 3 that the fillet connecting the two stages of combustion pressure rise tends to disappear as C.R. is raised. It is well rounded at a C.R. of 10 and extends over 10° of crank angle which is the time taken by the second combustion pressure rise. The fillet scarcely exists at a C.R. of 12.8, diagram No. 4, and the time taken by the second pressure rise is then not greater than 4° of crank angle or 1.7×10^{-3} sec.

The diagram, Fig. 4, for rate of change of pressure with time, dp/dt , is complementary to diagram No. 2 of Fig. 3, and should be compared with it. Thus during compression, rate of change is nearly constant for approximately 12° of crank angle before the first combustion pressure rise which begins at 8° before t.d.c. The rate then increases but falls to zero at the end of the first period of combustion and the beginning of the second combustion pressure rise. It then rises to a maximum and falls to zero as the combustion pressure reaches a maximum at 10° after t.d.c. and expansion begins. Rate of change then increases again but with a negative value, rapidly at first and then relatively slowly until expansion is complete and rate of change becomes zero.

Indicator diagrams taken for relatively rich mixtures do not show a marked first pressure rise. The diagram of Fig. 5, taken at the Opt. C.R. of 10 when

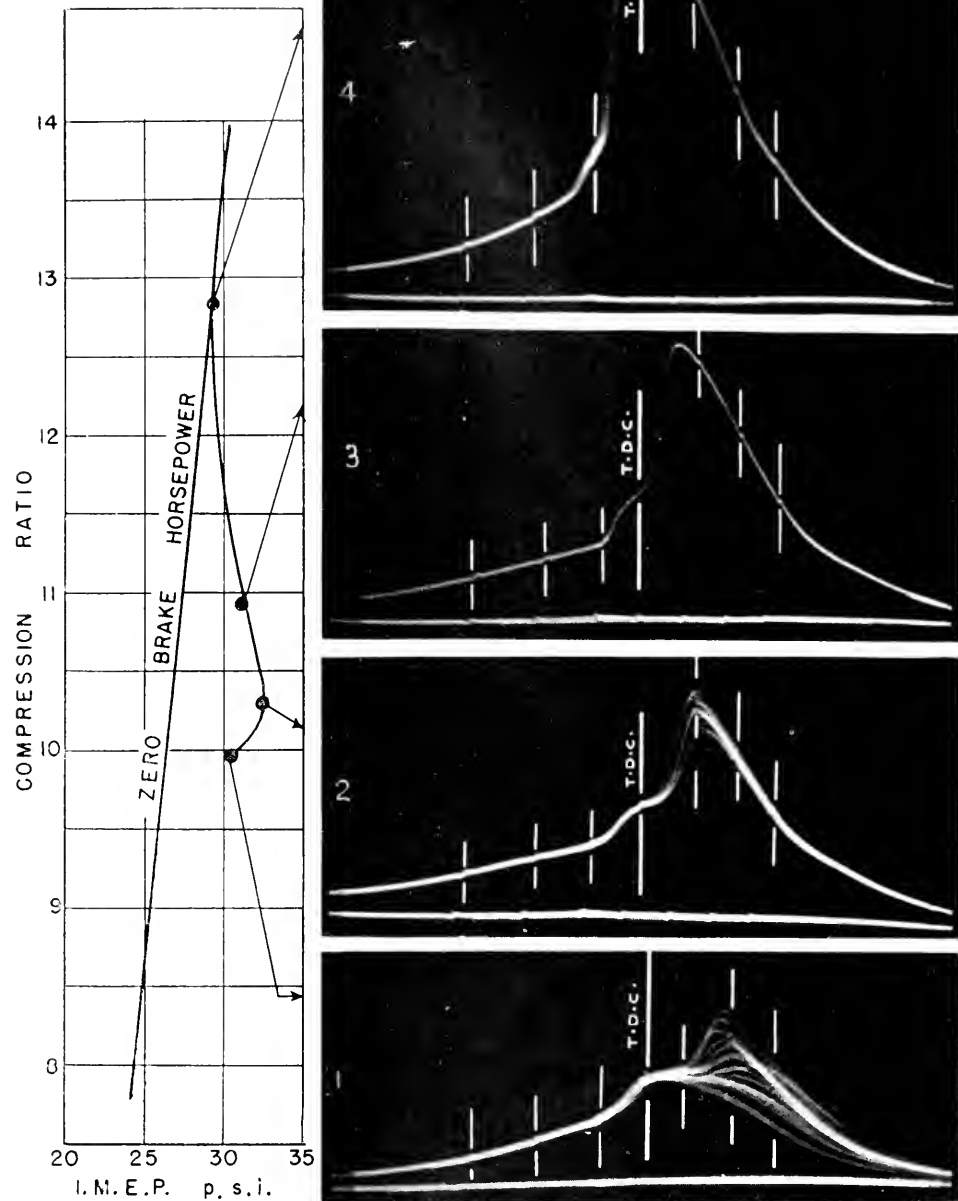


FIG. 3. Pressure-time indicator diagrams, showing two stage ignition, the advance in timing of maximum combustion pressure as C.R. is increased and the occurrence of maximum power output when combustion pressure is a maximum at 10° after t.d.c. Heptane-air mixture 70% weak, ignition by compression with blind plugs.

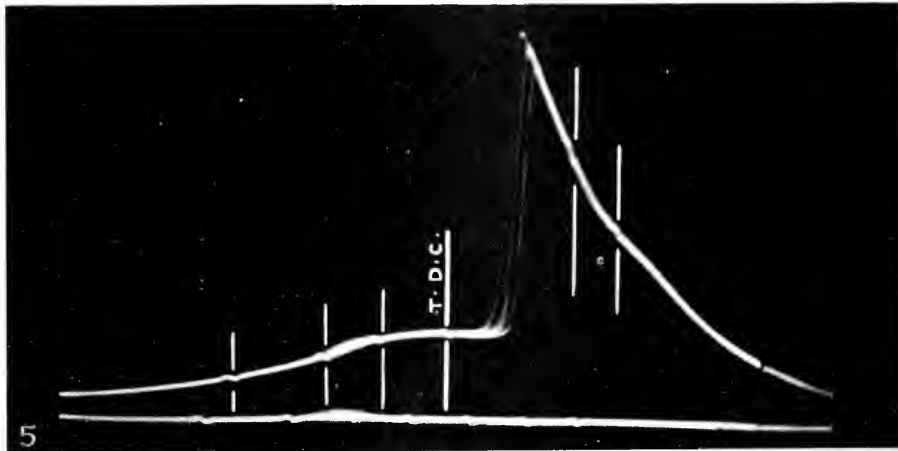
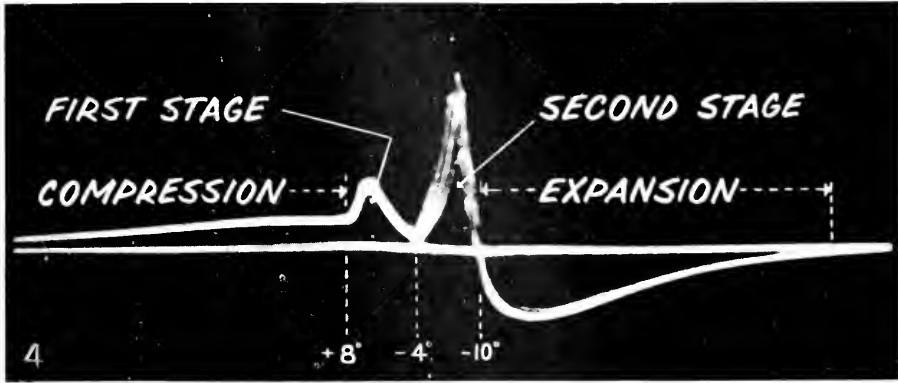


FIG. 4. Rate of change (dp/dt) indicator diagram taken at Opt. C.R. and showing first stage of ignition, beginning at 8° before and ending at 4° after t.d.c., with maximum combustion pressure occurring 10° after t.d.c. Heptane-air mixture 70% weak, ignition by compression with blind plugs.

FIG. 5. Pressure-time indicator diagram taken at Opt. C.R. with a nearly correct heptane-air mixture and showing a single stage ignition with maximum combustion pressure occurring at 10° after t.d.c. Ignition by compression with blind plugs.

using a nearly correct pentane-air mixture shows only a slight first pressure rise between 20 and 10° before t.d.c. Thus the pressure time line is nearly horizontal from 10° before t.d.c. to the beginning, at from 6 to 9° after t.d.c., of the extremely rapid combustion pressure rise. It will be noted that the diagram includes three cycles which do not repeat exactly in respect of the time of occurrence of the combustion pressure rise.

The Relation Between Opt. C.R. and M.S. With Ignition by Compression and the Effect of Charge Density

It is apparent from the experimental results exhibited by Figs. 1 and 2 that a graph drawn through the Opt. values of C.R. would be of a W form similar to that obtained when using acetaldehyde and diethyl ether as engine fuels in the standard conditions of the new method of experiment (6). The broken line graphs of Figs. 1 and 2 drawn accordingly are necessarily of a distorted W form because they are plotted on a base of power developed and the relation between power and M.S. is not linear as mentioned earlier.

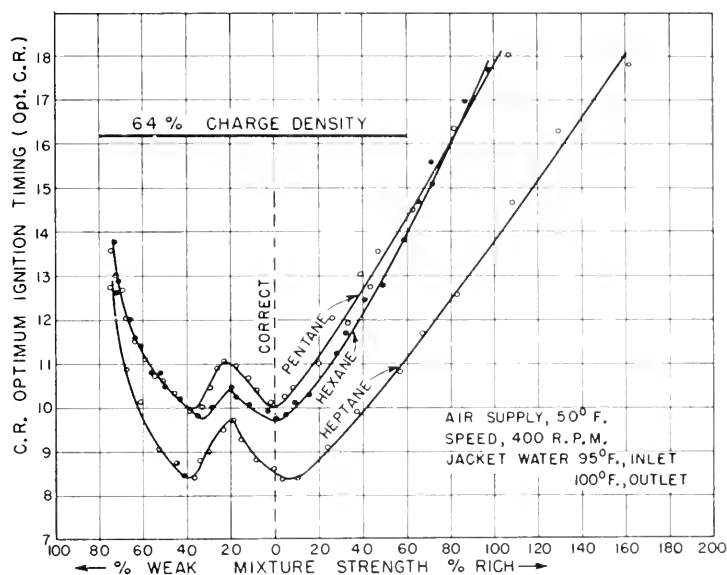


FIG. 6. Relation between Opt. C.R. and mixture strength at 64% of normal charge density. Experiments with heptane, hexane, and pentane. Ignition without spark plugs.

The experiments presently to be described were made in the conditions used for those with acetaldehyde and diethyl ether and similarly with blind steel plugs replacing the spark plugs and bouncing pin. Pentane, hexane, and heptane were used as fuels at two charge densities, namely, 64 and 78% of normal and with values of M.S. ranging from 76% weak to over 100% rich. The C.R. was adjusted for maximum power at every M.S. used. The experimental results obtained at 64% of normal charge density are exhibited by the graphs of Fig. 6; those obtained at 78% by the graphs of Fig. 7. The graphs are plotted on a

M.S. base and are always of a nearly symmetrical W form, with two minimum values of Opt. C.R. and an intermediate maximum. A minimum occurs for mixtures 40% weak and again for the correct mixture. The intermediate maximum occurs for mixtures 20% weak. The percentages as applied to the three fuels and the two charge densities are approximate. The W form is most pronounced for the heptane-air mixtures for which both minimum values of Opt. C.R. were 8.4 at 64% of normal charge density, Fig. 6, and 8.1 at 78%, Fig. 7. The minimum values of Opt. C.R. for pentane were equal at 10, at the lower charge density, but at the higher, Opt. C.R. for the first minimum was 9.7 and 9.5 for the second. These small differences and similar ones observed when using hexane at differing charge densities are probably within the accuracy of measurement because they have been found to vary with the degree of piston and cylinder wear, the surface condition of the combustion chamber and the time taken between changes of M.S. for the stabilization of surface temperatures in the combustion chamber.

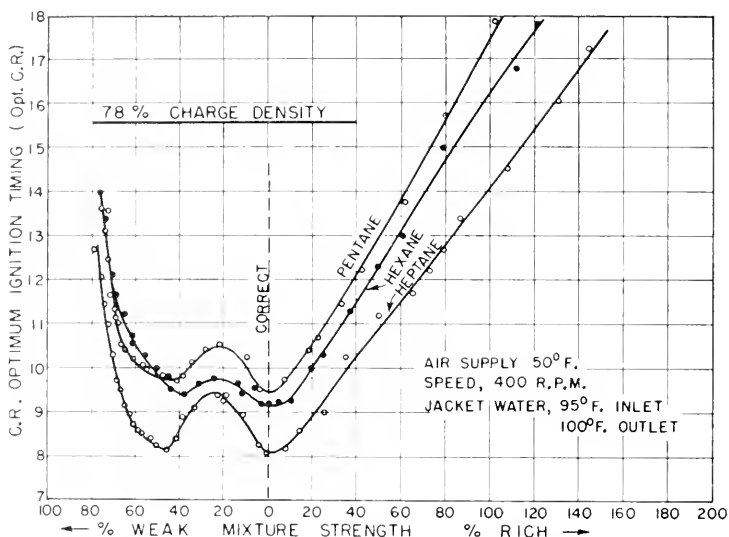


FIG. 7. Relation between Opt. C.R. and mixture strength at 78% of normal charge density. Experiments with heptane, hexane, and pentane. Ignition without spark plugs.

The effects of increasing charge density from 64 to 78% of normal were, as is shown by a comparison of the graphs of Figs. 6 and 7 to lower the values of Opt. C.R. over the entire range of M.S., except in the case of rich heptane-air mixtures, and to move the minimum and maximum values of Opt. C.R. slightly to weaker mixtures. Knock intensity for particular values of M.S. increased on increasing charge density. The small differences due to the relatively small change of charge density were difficult to measure accurately for the reasons mentioned above.

Power and Thermal Efficiency With Compression Ignition and Optimum Compression Ratio

Relevant data are available from the results of the experiments with pentane, hexane, and heptane made at two charge densities. The results of the six sets of experiments are, however, similar in character and it will suffice for the present to describe those obtained when using pentane at 64% of normal charge density with M.S. ranging from 74% weak to 107% rich. Data for indicated and brake horsepower are given by the graphs of Fig. 8 and for indicated and brake thermal efficiencies by those of Fig. 9. A graph for the relation between Opt. C.R. and M.S. is given on both figures for convenience of reference.

The results exhibited by the graphs of Fig. 8, show that while maintaining optimum nuclear ignition timing, it was possible to reduce M.S. until brake horsepower became zero. Maximum power, both indicated and brake, was obtained with the correct mixtures and on increasing M.S. to be 107% rich, indicated power diminished by 6% only from the maximum. A greater percentage decrease of brake power occurred because friction loss increased from 0.54 to 0.65 horsepower on increasing the C.R. from 10 to 18.

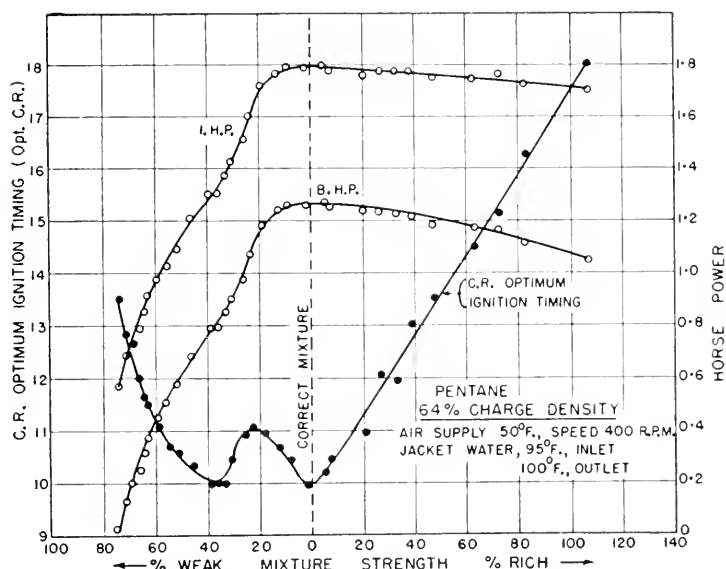


FIG. 8. Indicated and brake horsepower at Opt. C.R. and 64% of normal charge density for pentane-air mixtures ranging from 75% weak to 105% rich. Ignition without spark plugs.

The results exhibited by the graphs of Fig. 9 show that indicated thermal efficiency attained a maximum of 41% for a mixture 60% weak used at an Opt. C.R. of 17. A maximum of 25% was obtained for brake thermal efficiency when the mixture was 20% weak at an Opt. C.R. of 11. The thermal efficiencies are regarded as high values in view of the relatively low charge density and the correspondingly large proportion of the heat of combustion lost to the cool

surfaces of the combustion chamber which has relatively large surface to volume ratio at the high values of C.R. required for optimum compression ignition timing. It is difficult when using the extremely weak mixtures required for maximum thermal efficiency, and with brake horsepower approaching zero, to maintain experimental conditions sufficiently steady for a high degree of accuracy of measurement. Thus it will be noted that the experimental points for indicated thermal efficiency do not all lie on the graph. The irregularity is attributed to inaccurate measurement of the horsepower absorbed by mechanical and fluid friction which is added to the observed brake horsepower to obtain the indicated value. Thus it will be seen that values for brake horsepower, Fig. 8, obtained by direct measurement, fall well on the corresponding graph.

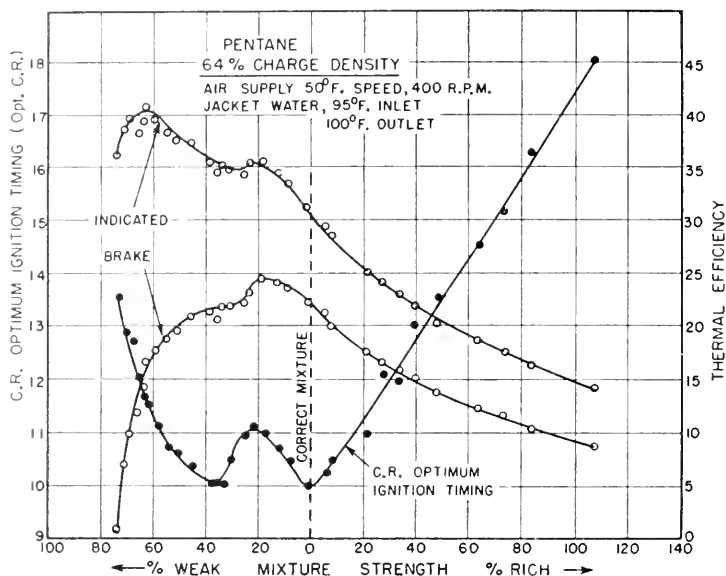


Fig. 9. Indicated and brake thermal efficiency at Opt. C.R. and 64% of normal charge density for pentane-air mixtures ranging from 75% weak to 105% rich. Ignition without spark plugs.

The Initiation of Nuclear Ignition by an Unfired Spark Plug

The ignition of the fuel air mixture by compression after blind plugs had replaced the spark plugs and bouncing pin occurred only at relatively high compression ratios and was attributed, in Part XIX (6), to ignition being then made possible by decomposition of the fuel during compression to yield nuclear centers of ignition. Furthermore, it was suggested in Part XX (3) that nuclear ignition of the entire charge, instead of the end gas only, could be due to a pressure wave started by the preferential nuclear ignition of a small volume of mixture adjacent to an overheated surface such as an exhaust valve. It may safely be assumed that the exhaust valve was the hottest surface in the combustion chamber when no spark plugs were used and that a still hotter surface was

provided on the replacement of a blind steel plug by the ceramic core of an unfired spark plug. It therefore became of interest to determine the characteristics of nuclear ignition when one of the blind plugs was replaced by an unfired spark plug.

The ceramic core of most types of spark plug is known to attain a higher temperature than the exhaust valve, and the plug used for the experiments was Champion No. 8, which is specified for use with the C.F.R. knock testing engine. The length of the exposed part of the ceramic core is $\frac{7}{8}$ in. The plug was always used in the standard position in the wall of the combustion chamber, midway between the exhaust and inlet valves and diametrically opposite the bouncing pin position.

Heptane was used for the first series of experiments, made when using mixtures ranging from 60% weak to 30% rich, with the object of determining corresponding values of Opt. C.R., with no spark plug, with one unfired spark plug, and with the spark plug fired at 10° in advance of t.d.c. Charge density was 78% of normal. The experimental results are exhibited by the graphs of Fig. 10.

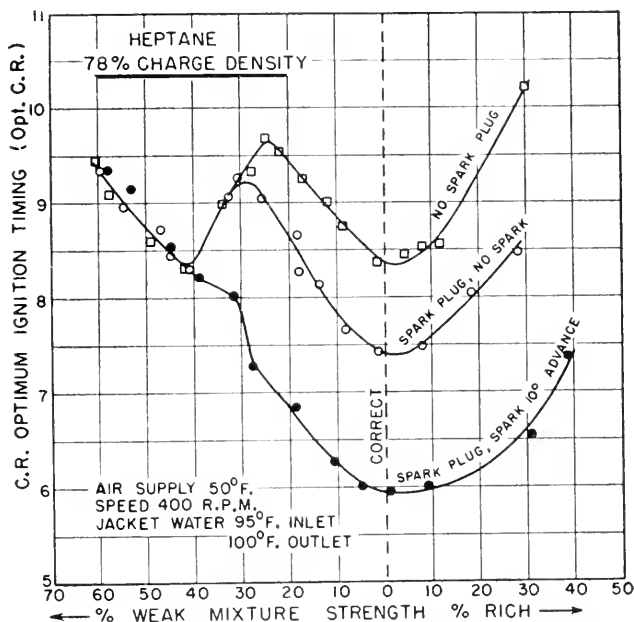


FIG. 10. Relation between Opt. C.R. and mixture strength with ignition by compression without spark plugs, with one unfired plug, and by a plug fired at 10° before t.d.c. Heptane-air mixtures, 78% of normal charge density.

The upper graph of the figure is for results obtained when the spark plugs and bouncing pin were replaced with mild steel blind plugs. The combustion chamber surface of maximum temperature was then that of the exhaust valve and the graph showing the relation between Opt. C.R. and M.S. is of the W form as described earlier and is similar to that obtained in similar conditions

when acetaldehyde and diethyl ether were used as engine fuels, Part XIX (6). There are two minimum values of 8.4 for Opt. C.R., one for a mixture 40% weak and another for the correct mixture. The intermediate maximum value is 9.7 for a mixture 25% weak.

The middle graph of the figure is for results obtained when an unfired spark plug in the standard position replaced a blind plug. It is evident from a comparison of the upper and middle graphs that the unfired plug possessed an igniting effect which became apparent with mixtures richer than 30% weak. Thus when the M.S. was increased to be correct, the corresponding Opt. C.R. was 8.4 with no spark plug and 7.4 with an unfired plug. The igniting effect of the unfired plug continued to increase with increase of M.S. and for a mixture 30% rich, reduced the value of the corresponding Opt. C.R. from 10.2 to 8.6.

The results obtained when the spark plug was fired 10° in advance of t.d.c. are shown by the lower graph of Fig. 10. It is of the conventional U shape over the range of mixture strength for which spark ignition was effective, with Opt. C.R. for the correct mixture having the relatively low value of 5.9.

The igniting effect of an unfired spark plug was again demonstrated by a series of experiments with pentane made in the conditions similar to those used for heptane but over a wider range of mixture strength, extending from 75% weak to over 100% rich. The results are given by the two sets of graphs of Fig. 11. The upper set is for the relation between indicated thermal efficiency and M.S.; the lower is for the relation between Opt. C.R. and M.S.

It will be seen by reference to the lower set of graphs that the characteristics of nuclear ignition at Opt. C.R., with and without an unfired spark plug, are similar to those determined for heptane-air mixtures as shown by the graphs of Fig. 10, but values of Opt. C.R. are approximately 1.5 ratios higher. It was mentioned when describing the similar experiments with heptane that the igniting effect of the unfired plug increased as M.S. was increased to be 30% rich. A similar effect was obtained with pentane as shown by the graphs of Fig. 11, but it will be noted that the igniting effect tended to diminish as the M.S. was further increased to be 100% rich.

The lower graph of Fig. 11 which exhibits the results obtained when the spark plug was fired is, as for the similar experiments with heptane, of symmetrical U shape over the greater part of the range of mixture strength for which spark ignition is effective. It is, however, a narrower U and displaced toward relatively rich mixtures. Thus the minimum value of Opt. C.R. for pentane was 6.0 for a mixture 10% rich while that for heptane was 5.9 for a correct mixture, but for mixtures 30% weak, Opt. C.R. for pentane was 1.5 ratios higher than for heptane.

It is of interest that the three graphs of Fig. 11, for the relation between Opt. C.R. and M.S. tend to coincide only as the mixture becomes extremely rich while the graphs for related *indicated thermal efficiencies* do coincide for mixtures more than 40% rich, although Opt. C.R. is then 7.1 with spark ignition, 10.1 with the spark plug unfired, and 12.7 with no spark plug. On the other hand,

the graphs for thermal efficiencies do not coincide over the mixture range 40 to 60% weak although the related values of Opt. C.R. are identical within the accuracy of experiment. There is, however, an apparent tendency for the values of thermal efficiency to coincide for mixtures leaner than 60% weak.

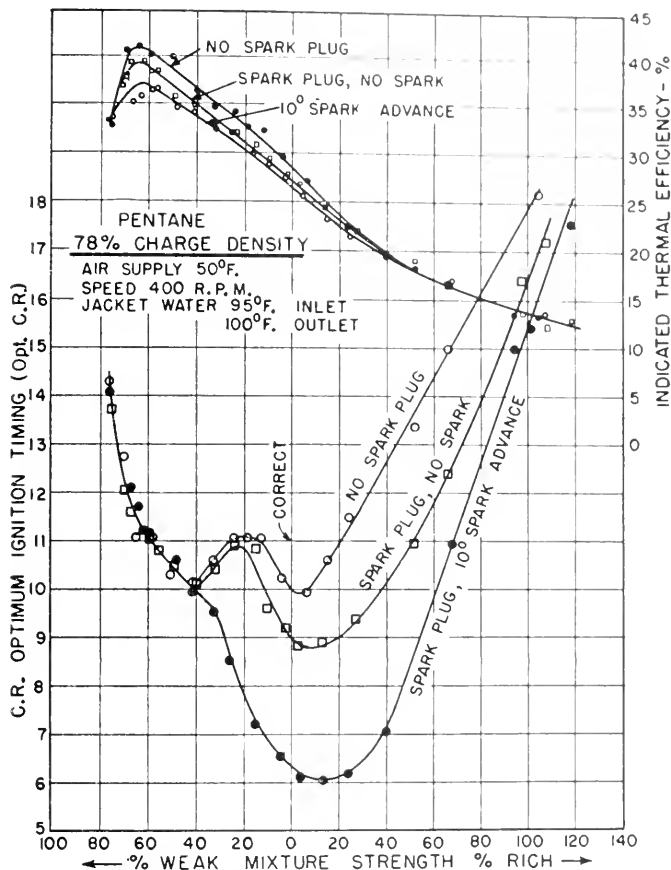


FIG. 14. Relation between Opt. C.R. and mixture strength with ignition by compression without spark plugs, with one untired plug, and by a plug fired at 10° before t.d.c. Also graphs for corresponding values of indicated thermal efficiency. Pentane-air mixtures, 78% of normal charge density.

The Transition From Spark to Compression Ignition

A transition from ignition by spark to ignition by compression as M.S. is reduced and C.R. increased to maintain an optimum value has been found by experiments already described, to occur solely when using fuels which in the corresponding temperature and pressure conditions decompose thermally to form material nuclei of ignition. The transition has always occurred within the M.S. range 40 to 50% weak when spark ignition timing was fixed at 10° in advance of t.d.c. The particular spark ignition timing was chosen merely as a

reasonable value for early experiments with acetaldehyde and was retained for comparable experiments with other liquid fuels. It therefore became of interest to determine whether the transition always occurred within the same range of M.S. when spark ignition timing was set later or earlier than 10° advance and whether a spark timing other than 10° in advance of t.d.c. should have been used.

The results of four sets of experiments made accordingly when using spark settings of 20, 15, 10, and 5° in advance of t.d.c. are given by the graphs of Fig. 12. Heptane was used as the fuel with charge density 78% of normal. Broken line graphs for compression ignition with the spark plugs replaced by blind plugs and with one plug unfired, as reproduced from Fig. 10, have been added to the figure.

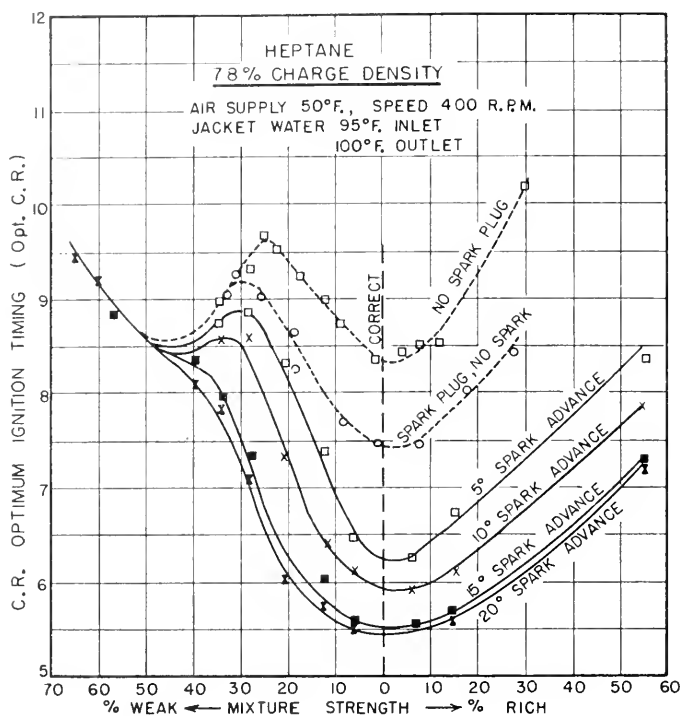


FIG. 12. Relation between Opt. C.R. and mixture strength with spark ignition at 5 to 20° before t.d.c. Heptane-air mixtures, 78% of normal charge density.

The graphs of the figure show that the relation between Opt. C.R. and M.S. tends rapidly to become unaffected by spark timing as M.S. is reduced to be leaner than 40% weak until with a mixture 48% weak the effect of spark timing is nil. Then as M.S. is further reduced ignition can be continued by the progressive increase of C.R. as required to maintain the optimum value.

The tendency of the graphs for spark ignition of mixtures leaner than 30% weak to assume the form of those for nuclear ignition, as spark timing is retarded, is of interest in respect of the nuclear theory. Thus when spark ignition is fixed

at only 5° in advance of t.d.c. and C.R. raised to *the optimum value*, combustion must be completed by approximately 10° after t.d.c., that is, 15° after the spark had passed. This is an impossibly brief interval in the usual circumstances of spark ignition. The probable explanation is that at the relatively high values of Opt. C.R. required for the effect, decomposition of the fuel had provided a concentration of nuclei sufficient for an exceptionally rapid propagation of the flame started by a spark but not sufficient for autoignition. It is difficult to obtain repeatable experimental results for the relation between Opt. C.R. and M.S. within the range of M.S. for which spark ignition is succeeded by compression ignition, even when the combustion chamber of the engine has been cleaned before beginning a set of experiments. The difficulty diminishes as spark timing is advanced but exists even with the 10° advance generally used for the experiments recently described. Thus referring to the preliminary experimental results of Fig. 10, it will be seen that the graph for 10° spark ignition advance exhibits an inflection only, over the mixture range 30 to 40% weak, whereas the similar graph, Fig. 12, obtained in like conditions and also with heptane, exhibits a definite reversal of direction.

The experimental results confirm that, irrespective of timing, spark ignition tends to become ineffective, in the conditions of the experiments, for mixtures leaner than 30 to 40% weak and completely so for those leaner than 50% weak. They show also that in the conditions of the experiments, the rate of change of Opt. C.R. with M.S., when spark ignition is used, is substantially independent of spark timing over a wide range of M.S. on both the weak and rich side of the correct value.

Compression Ignition as Affected by an Unfired Spark Plug With and Without Electrodes

Premature ignition in a carburetor engine running on spark ignition is frequently attributed to the electrodes of the spark plug having become incandescent. There was no evidence of that igniting effect having occurred in the temperature conditions of the experiments described in this and preceding parts, and it has been assumed accordingly that the ceramic core of the plug, not the electrodes, was responsible for the decrease of Opt. C.R. observed when a blind plug was replaced by an unfired spark plug, nevertheless, in order to remove any doubt, compression ignition experiments were carried out with an unaltered C.F.R. Champion No. 8 spark plug in the standard position and repeated immediately, after removal of the electrodes. Experiments were made with M.S. varied over the range for which significant results had been obtained when using an unfired spark plug as shown by the graphs of Figs. 10 to 12.

The experimental results are given by the graphs of Fig. 13. The broken line graphs are for results obtained with the unfired and unaltered spark plug set in the standard position. Experimental points are omitted in order to avoid confusion. The results obtained after removal of the electrodes are given by the marked experimental points. It is demonstrated accordingly that the igniting effect of an unfired spark plug as observed in the conditions of the compression ignition experiments of this Part is due to the ceramic core.

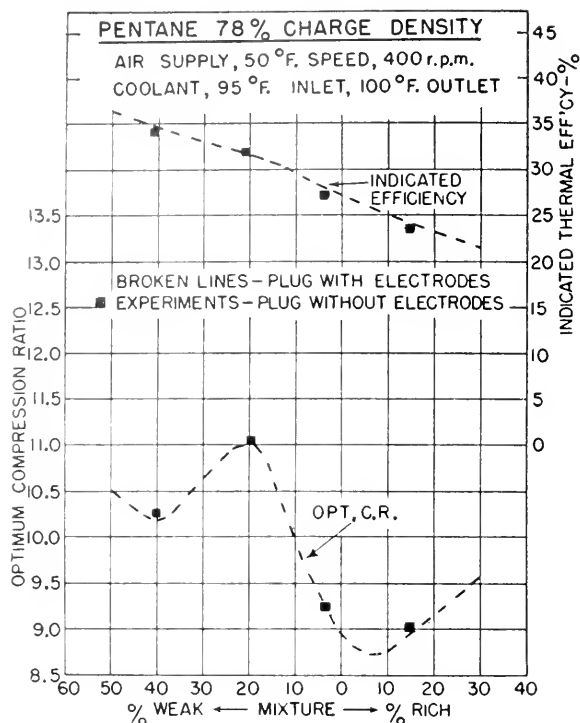


FIG. 13. Relation between Opt. C.R. and mixture strength and between Opt. C.R. mixture strength and indicated thermal efficiency, with an unfired spark plug with and without electrodes, in standard position. Pentane-air mixtures, 78% of normal charge density.

Maximum Combustion Pressures, Compression, and Spark Ignition

The maximum pressure attained in an engine cylinder can be measured by a Bourdon gauge, when a check valve is placed in the passageway connecting it with the cylinder. The Keine Indicator* has been developed accordingly for the continuous indication of the maximum values of Diesel engine combustion pressures. The makers co-operated in providing the special features required for the fitting of the instrument to the C.F.R. engine for the measurement of a wide range of maximum pressures including the exceptionally high pressures accompanying early preignition. These have frequently been of the order of 1800 p.s.i.

The passageway from the check valve to the cylinder, which must be surrounded by a length of cooling fins, was of the minimum practicable diameter, namely 1/16 in., in order that the volume would be small relative to that of the combustion chamber of the C.F.R. engine at exceptionally high compression ratios. The check valve was especially designed to withstand the high temperatures and pressures accompanying preignition while maintaining accuracy of seating. A special valve of a double seating type was supplied for the closure of the connection from the cylinder to the check valve in order that the indicator

* Keine Diesel Accessories Inc. 10352 Pacific Ave., Franklin Park, Ill., U.S.A.

might be used in the course of a trial only as required. When the indicator was used for experiments described in this Part, maximum combustion pressure was observed after C.R. had been adjusted to the apparent optimum value, which was then corrected for the volume of the passageway connecting the indicator to the cylinder. The results of a typical set of experiments made with heptane as the fuel, charge density being 64% of normal, are given by the graphs of Fig. 14.

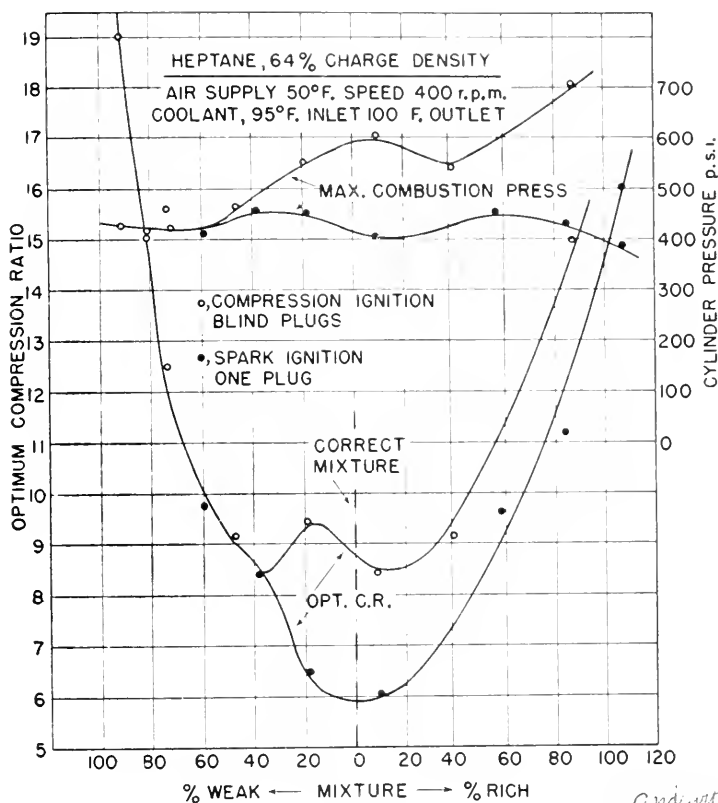


FIG. 14. Maximum combustion pressure at Opt. C.R. with compression ignition before t.d.c. Heptane-air mixtures, 64% of normal charge density *and with spark ignition at 10°*

The characteristics of maximum combustion pressures as exhibited by the graphs of the figure are as would be expected from the results of ignition experiments described earlier in this Part and from considerations based on the nuclear theory of ignition, and it is shown by the graphs that maximum combustion pressures for mixtures leaner than 50% weak have the same value with or without spark ignition. On the other hand, maximum combustion pressures for very rich mixtures increase rapidly as M.S. is further increased if ignition is by compression, but decrease when ignition is by spark, as would be expected from the results of corresponding compression and spark ignition experiments given by the graphs of Fig. 12.

The ignition by compression of rich mixtures, which tend to run "cool" in an engine, requires a relatively high C.R. for the formation of the concentration of nuclei necessary for ignition, and rate of flame propagation after ignition occurs must be correspondingly rapid. Thus an explanation is afforded for the extremely high maximum pressure and the accompanying heavy combustion knock, observed in the circumstances.

The experimental results for maximum combustion pressures can be applied to correlate charge density and knock intensity. The charge density, in terms of volumetric efficiency, was 64% of the normal 85%, that is, it was 54% of the 100% volumetric efficiency which would require some degree of supercharging for its attainment. It can be assumed that absolute combustion pressures increase directly with increase in charge density if the effect of surface temperatures be neglected. Thus considering the correct mixture, maximum combustion pressure with spark ignition was 425 p.s.i., absolute; an experimental value which includes pressure losses due to reactions depending on the increase of temperature. Therefore, at the normal volumetric efficiency of 85% and in accordance with the assumption mentioned, maximum combustion pressure would have been 665 p.s.i. (gauge), and 775 p.s.i. (gauge) at 100% volumetric efficiency. Similarly, when ignition was by compression, Opt. C.R. being 8.8, the experimental value of maximum combustion pressure was 590 p.s.i. (gauge) and the respective maximum values would have been 955 and 1115 p.s.i. (gauge) at 85 and 100% volumetric efficiency, if it were then possible to adjust C.R. to an optimum value.

An estimate of the knock intensities corresponding to the maximum combustion pressure mentioned above can be made by reference to the graphs of Fig. 2. Thus it will be seen, for example, that when using a 10% rich heptane-air mixture at 64% of normal charge density, the Opt. C.R. being 8.65, knock intensity was described as "medium". The maximum combustion pressure in the circumstances, according to the corresponding graph of Fig. 14, was 600 p.s.i. It is evident, therefore, that if charge density were increased even to the normal value, maximum combustion pressure would be expected to increase to 955 lb. p.s.i. and an investigation of the characteristics of compression or nuclear ignition would be prevented by the severity of combustion knock.

Lower Limit of Inflammability, Pentane

It has been shown that in the conditions used for experiments with pentane, hexane, and heptane, described in this Part, spark ignition becomes ineffective for mixtures leaner than approximately 45% weak but that a wide range of still leaner mixtures are ignitable by compression; an effect attributed to nuclear ignition. Thus the experimental results, Fig. 8, show that when pentane was used as the fuel for the C.F.R. engine, charge density being 64% or normal, it was possible to reduce mixture strength until brake horsepower became nearly zero, provided C.R. were adjusted continuously to the optimum value. Although M.S. was then 74% weak it was apparent that the lower limit of inflammability had not been attained.

The first attempt to determine the possible lower limit was made at a time when cylinder wear had become excessive. The results were however of considerable interest and are given by the graphs of Fig. 15. B.H.P. became zero when the pentane-air mixture was 81% weak, I.H.P. was then 0.58, which is the H.P. required to overcome friction and pumping losses. Then by using the dynamometer to supply power to compensate in part for the losses, it became possible to reduce M.S. to 96% weak and I.H.P. to 0.07. The dynamometer then supplied 0.54 H.P. leaving 0.07 H.P. to be supplied by combustion of the fuel. It was a small margin but appeared to be real, because engine speed decreased when the fuel supply was stopped and an increased supply of power by the dynamometer was then required to maintain the speed at 400 r.p.m.

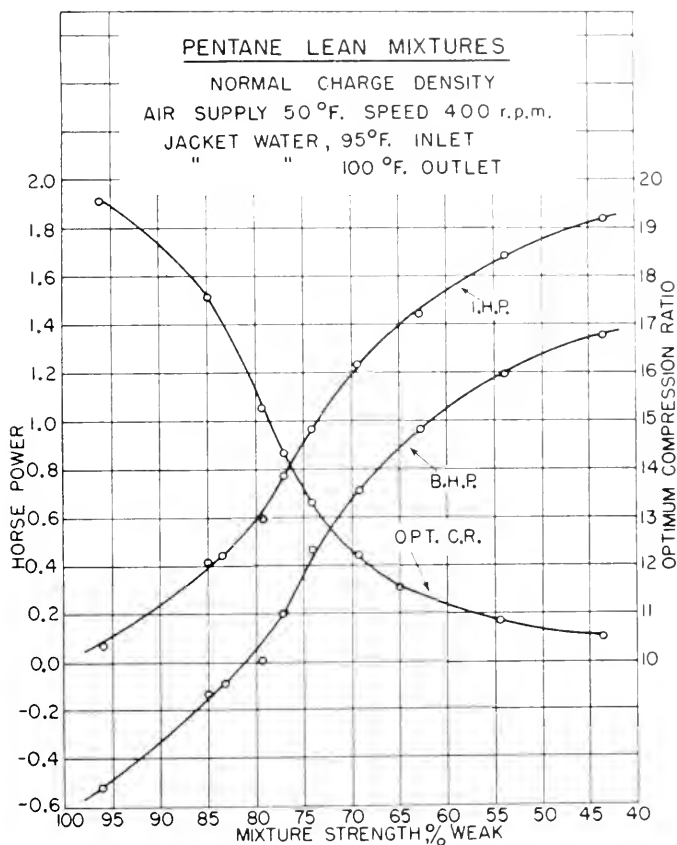


FIG. 15. Results of experiments with pentane-air mixtures leaner than 10% weak, made to determine lower limit of inflammability. Ignition by compression, no spark plugs. Normal charge density.

The mixture 96% weak contained 4% of the fuel required for the correct air to pentane ratio of 15.3:1, by weight. Ignition was therefore obtained with an air to pentane ratio of approximately 370:1 by weight.

Limits of inflammability are given usually in terms of the percentage of the vapor of the combustible in a mixture with air. Thus the lower limit of inflammability of a pentane-air mixture ignited by a spark at atmospheric pressure is given by Coward and Jones (1, p. 125) as 1.4. The mixture is then 45% weak and it will be remembered that spark ignition in the engine failed when M.S. was reduced so that it was approximately that value, no allowance being made for the effect of temperature and pressure or for the effect of dilution of the mixture with residual gas. It is possible that one effect compensated for the other.

The ultimate lower limit, attained by compression ignition when the pentane-air mixture was 96% weak, was 0.104 as compared with that of 1.4 given by Coward and Jones for ignition by spark.

The accuracy of the results for the ultimate lower limit may have been affected by the combustion of lubricating oil. The engine, as already mentioned, was not in first class condition and a thin oil, S.A.E. 10 — 10W, was used in order to reduce piston friction in the cool conditions of operation. The engine was, however, not "running on oil" even when M.S. was nominally 96% weak because speed diminished when the pentane supply was stopped. It is nevertheless indicated by the unusual double inflection in the graph, Fig. 15, for the relation between Opt. C.R. and M.S., that the oil may have constituted an appreciable part of the combustible mixture when it was leaner than 85% weak.

Lower Limit of Inflammability, Heptane

The experiments were made with mixtures leaner than 40% weak. It was possible, therefore, to use normal charge density and thus obtain a greater power output for a particular M.S. than when charge density was subnormal, with a corresponding improvement in regularity of combustion as the lean mixture limit was approached. Special care was taken to reduce the quantity of oil passing into the combustion chamber by using a cylinder and piston in nearly new condition and by fitting new rings to the piston.

Experimental results are given by the graphs of Fig. 16, for the relations between M.S. and Opt. C.R., indicated thermal efficiency, I.H.P., and B.H.P. A maximum value of 42% was obtained for indicated thermal efficiency at a M.S. of approximately 68% weak. B.H.P. was zero at a mixture 84% weak and I.H.P. was then 0.45. The leanest mixture with which continuous operation was possible was 93% weak and Opt. C.R. was then 22.8 and the corresponding lower limit of inflammability was 0.133 as compared with the value of 1.0 given by Coward and Jones (1, p. 125) for a heptane-air mixture ignited by a spark at atmospheric temperature. A mixture 93% weak contains air to fuel in the ratio of 220:1 by weight.

Decomposition Products of Fuel Which Remain on Surfaces of the Combustion Chamber

Nuclei of ignition dispersed throughout the combustible mixture consist, according to the modified nuclear theory of ignition (2), of the products of the thermal decomposition of the fuel. The nuclei are necessarily molecular aggre-

gates and may be assumed to vary in size especially when concentration of fuel in the mixture with air is not uniform. It is to be expected that the smaller ones could be oxidized without liberating sufficient heat to start a flame and that some proportion only of the larger ones would survive combustion. These, in large proportion, would be carried out with the exhaust but some might remain as deposits on relatively cool surfaces in the combustion chamber. These deposits when found in the combustion chamber can be attributed to decomposition of the fuel solely if the cylinder, piston, and rings are in such good condition that the least possible amount of lubricating oil passes into the combustion chamber. This condition is of the utmost importance when an endeavor is made to observe deposits remaining after the use of mixtures containing fuel in extremely small concentration.

Inspections of deposits remaining in the combustion chamber were always made after ignition had been by compression, with blind plugs used in place of the spark plugs and the bouncing pin and when compression ratio had been adjusted to the optimum value for any particular M.S. Engine speed was always 400 r.p.m.; air supply temperature 50°F. and jacket coolant 95 to 100°F.

The first series of inspections was made when heptane was being used as the fuel with a charge density 78% of normal. After a 60% weak mixture had been used for a period just long enough to obtain steady running conditions, the water cooled surfaces of the combustion chamber were found to be coated with a brown deposit. It was little more than a color which could be wiped off easily from the smooth surfaces of the blind plugs, but appeared again after the briefest possible running period. The color did not appear on the warmer surface of the piston, which remained clean and dry. No other type of deposit was observed on increasing mixture strength until Opt. C.R. had passed through the first minimum value of 8:1, see Fig. 7., and attained the intermediate maximum of 9.4. The mixture was then 20% weak and observation disclosed the presence on the piston crown of scattered particles of carbon which reflected light from the inspection lamp and patches of carbon on the blind plugs. The next inspection, made after using the correct mixture, for which the second minimum Opt. C.R. occurred, disclosed a very thin and patchy layer of black carbon on the piston crown and a nearly uniform layer on the blind plugs. The layers became uniform and increased in thickness as M.S. was further increased. The carbon was always of the nonadherent type and black smoke appeared in the exhaust.

The immediate deposition of a brown color on relatively cool surfaces in the combustion chamber was of especial interest in that the phenomenon could not well be attributed to the decomposition or oxidation of lubricating oil. The engine was therefore dismantled, cleaned, and run for three hours with the mixture 60% weak. The first inspection made after running conditions had become steady disclosed that, as before, the brown color had appeared on relatively cool surfaces. It was especially evident on the blind plugs which could be removed for close inspection. The brown color appeared on the piston crown also, as the trial progressed, and at the end of the period of three hours a granular deposit which could be scraped but not blown off had formed.

On completion of the experiments with heptane made to determine the lower limit of inflammability at normal charge density, Fig. 16, the piston crown was found to be coated with a granular brown deposit, the water cooled surfaces and the inlet valve with a thin brown deposit and the exhaust valve with a thin white deposit. These experiments were begun with a mixture 40% weak and it seemed, therefore, that the deposits observed after the mixture had been reduced to 93% weak at the conclusion of the experiments might be residuals from deposits formed in the early stages of the experiments.

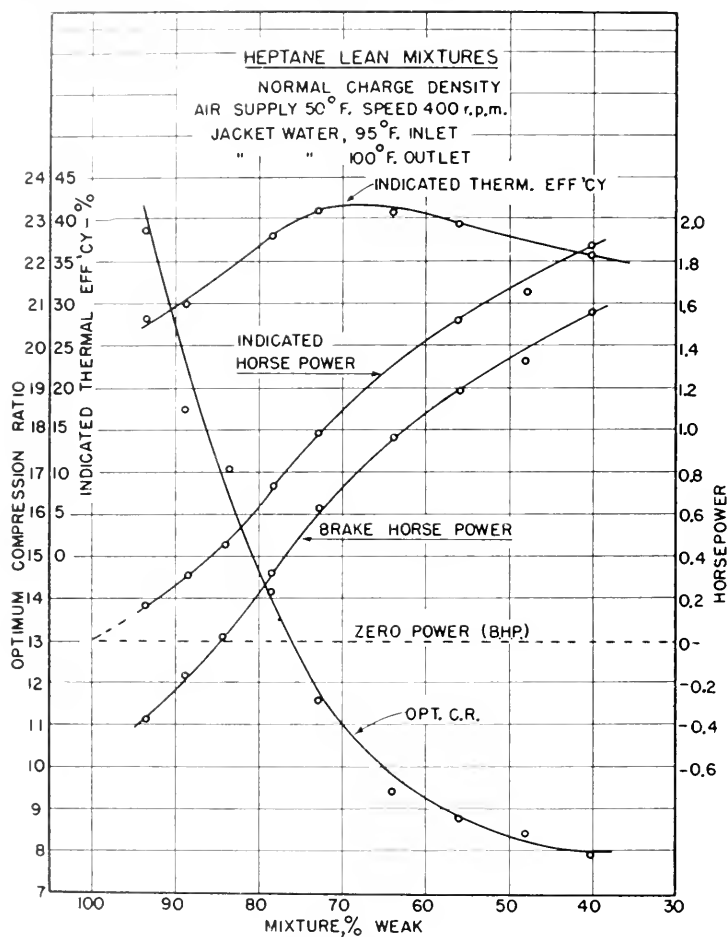


FIG. 16. Results of experiments with heptane-air mixtures leaner than 40% weak made to determine lower limit of inflammability. Ignition by compression, no spark plugs. Normal charge density.

It was decided, therefore, to begin a set of experiments with an extremely weak mixture and after the engine had been given a complete "top overhaul" it was run for two hours with a pentane-air mixture 65 to 70% weak. An inspection made at the end of the period disclosed that the exhaust valve was coated with

an extremely thin layer of a nearly white substance and that all other surfaces were clean. The M.S. was then increased to be 45 to 50% weak and the engine run for a period of four and one-half hours. The cylinder was then removed for a close inspection of all the combustion chamber surfaces. The blind plugs and portions of the other directly cooled surfaces were found to be coated with a dark brown substance, partly globular. There was a dark brown color on the inlet valve and the exhaust valve, as before, was thinly coated with a nearly white substance. The piston crown was thinly coated with a brown substance of a sticky and apparently resinous nature.

Deposits from the decomposition and oxidation of lubricating oil cannot occur in the M.I.T. compression ignition machine; nevertheless it was found by C. F. Taylor and associates (8, p. 241) that "in normal use the cylinder head and piston acquired a dark brown color. No attempt was made to remove this film except to wipe the surface with a clean linen cloth". In the course of experiments made earlier with the M.I.T. machine (7, p. 6), it was found that soot of a fine gossamer texture was deposited in the combustion chamber after explosion of rich isooctane mixtures.

Tizard and Pye (9, p. 115) when using a single stroke machine with a compression time of 0.14 sec. which is over 20 times longer than that of the M.I.T. machine, but regarded as "small" at the time, found that on compressing hydrocarbons and ether to temperatures well above that of ignition, carbon was thrown down even though oxygen was in excess. It was not recognized that the carbon was a product of the decomposition of the fuel. Their explanation that it was the result of preferential burning of the hydrogen of the molecules is not acceptable in view of the greater heat energy required to break the C-H than the C-C bonds.

The Effect of Engine Heat Load on the Characteristics of Ignition and Combustion

The combustible mixture entering the cylinder of a carburetor type engine in a state of high turbulence is brought into contact during induction and compression with surfaces that have been raised to relatively high temperatures by previous exposure to flame. The surface temperatures attained in steady running conditions depend on the heat load; defined as the heats of compression and combustion not converted into work or rejected with the exhaust. The surface temperatures attained accordingly vary with M.S. and C.R. if the other controlling factors, namely, engine speed, charge density, and the temperatures of the jacket coolant and the air supply remain constant. The surface temperatures would have maximum values at any particular C.R. when the mixture is correct. The surface of maximum temperature is probably that of the ceramic core of a "hot" variety of spark plug. That of the exhaust valve may be expected to attain a lower temperature and that of the central part of the piston crown a temperature still lower.

The "new method" of experiment is based on the "other factors" being selected to provide the minimum practicable heat load in an engine developing power, thus its effect on combustion characteristics can be shown only by

increasing it. An increase can be obtained by increasing engine speed but the experimental results would then not be comparable with those obtained at the speed of 400 r.p.m. selected as one of the standard conditions of the new method of experiment because the change of speed would not change heat load only. The heat load could be increased by increasing charge density but it would then not be possible to adjust C.R. to an optimum value over the range of M.S. which included the correct value because of the consequent severity of combustion knock. Experiments to demonstrate the effect of an increase of heat load were therefore made without change of conditions other than those of temperature. Thus the temperature of the jacket coolant was raised from a maximum of 100°F. to 212°F. and the mixture temperature raised to 300°F. These are the temperature conditions of the C.F.R.-A.S.T.M. motor method of knock rating.

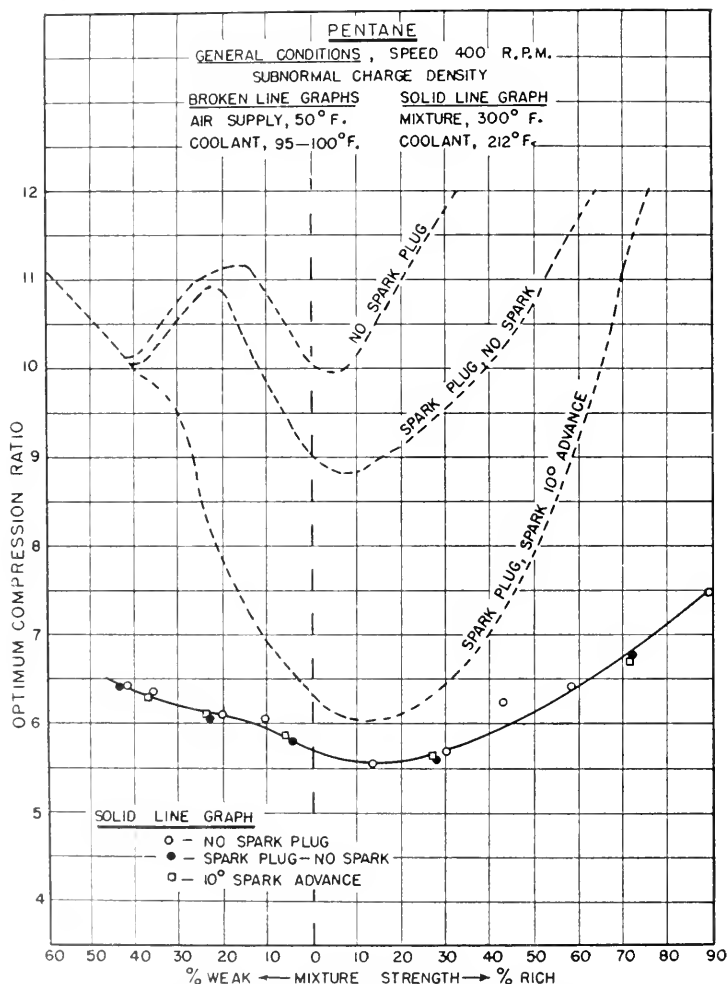


FIG. 17. Experimental results showing that on increasing heat load, the relation between Opt. C.R. and M.S. becomes independent of whether ignition is by compression with or without an unfired spark plug or by spark 10° before t.d.c. Pentane-air mixtures, subnormal charge density.

The experimental results obtained with the increased heat load, when using pentane as the engine fuel, are given by the solid line graph of Fig. 17. The broken line graphs of the figure are reproduced from Fig. 11, and are for results obtained with the relatively low heat of the new method of experiment. It is shown by the results given by the solid line graph that with combustion chamber surfaces at the temperatures due to a high heat load, the values of Opt. C.R. and necessarily the corresponding maximum values of thermal efficiency and power were obtained irrespective of the method of ignition. The broken line graphs show that with the relatively low heat load, which is an essential feature of the new method of experiment, it is possible to investigate on a comparable basis and over a wide range of mixture strength the separate effects on thermal efficiency and power of ignition by compression with and without an unfired spark plug in place and of ignition by spark.

The results of heat load experiments made when using heptane are exhibited by the graphs of Fig. 18. They are similar to those of Fig. 17 for pentane except that with the high heat load Opt. C.R. over the mixture range 30% weak to 30% rich, for compression ignition with no spark plugs in place, was somewhat higher

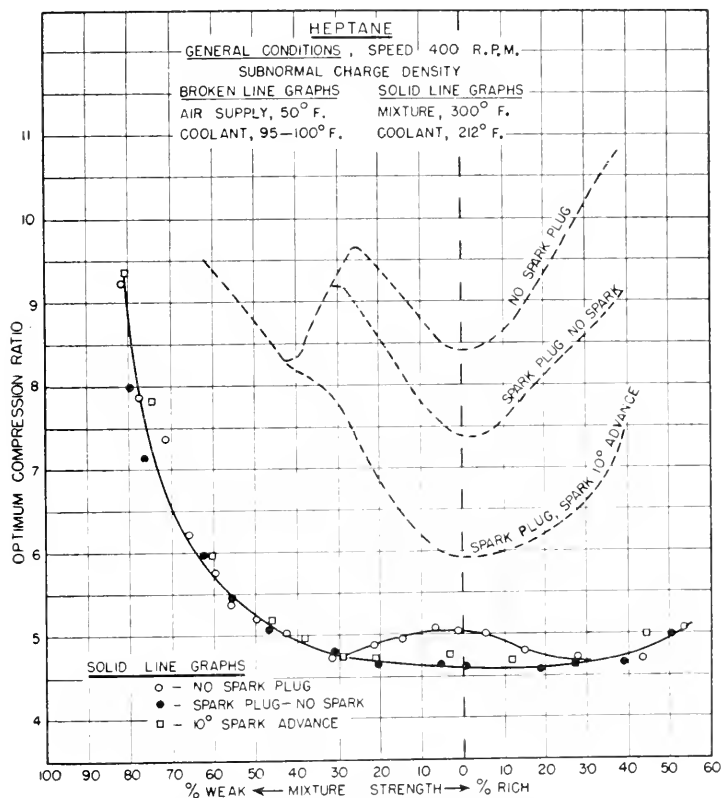


FIG. 18. Experimental results showing that on increasing heat load, the relation between Opt. C.R. and M.S. becomes nearly independent of whether ignition is by compression with or without an unfired spark plug or by spark 10° before u.d.c. Heptane-air mixtures, subnormal charge density.

than with one unfired plug or with ignition by spark. The difference was a maximum of 0.5 C.R. at correct mixture strength and indicates the beginning of a W form of graph. It is probable, in view of the experiments with spark ignition, Fig. 12, that lower values for Opt. C.R. with spark ignition would have been obtained if spark advance had been greater than the 10° used for the experiments. A further point of interest is that with subnormal charge density, a correct heptane-air mixture can be used at the Opt. C.R. of 4.5 even in the temperature conditions of the C.F.R.-A.S.T.M. motor method of knock rating.

DISCUSSION

The C.F.R. carburetor type engine became a compression ignition machine when operated in the conditions of the new method of experiment. The characteristics of combustion then obtained when using heptane, hexane, and pentane as engine fuels are similar to those described in Part XIX (6) with reference to experiments with acetaldehyde and diethyl ether. It was thus possible, with all five fuels, to operate the engine with ignition by compression over an extremely wide range of M.S. The graphs relating Opt. C.R. and M.S. were always of a W form when ignition was by compression and ignition by spark always failed for mixtures leaner than those within the range 40 to 50% weak. Moreover, it is obvious from the W form of the graphs that the relation between Opt. C.R. and thermal efficiency as affected by M.S., which was discussed at some length in Part XX (3) with reference to experiments with acetaldehyde and diethyl ether, is of the same character in respect of the normal paraffin fuels used for the experiments of this Part. The relation is of fundamental importance concerning the nuclear theory of ignition, the cause of detonation, and the mechanism of combustion in Diesel engines and will be discussed in a subsequent Part after some further investigation has been completed. It is possible, however, to state that the experiments with the normal paraffins indicate, as was shown by those with acetaldehyde and ether, that the departure of indicated from ideal values of thermal efficiency depends in part on the endothermic decomposition reactions required to produce nuclei of ignition in the combustible mixture of fuel and air.

Discussion will be concerned at present with other characteristics of combustion developed in the course of the experiments described in this Part and with the respective advantages for combustion research of the carburetor engine used as a compression ignition machine and the single stroke compression ignition machine. References will be made accordingly to the published data obtained by C. Fayette Taylor and associates (8) when using the single stroke machine developed by them in the Massachusetts Institute of Technology. These references will, for the sake of brevity, be to the "M.I.T. Machine".

Compression Ignition Conditions in the Engine and in the Single Stroke M.I.T. Machine

The engine, regarded as a compression ignition machine, differs from the single stroke variety as follows:—

The combustible mixture in the engine is diluted with exhaust gas to an extent depending on C.R. and the "delay period" must be considered as beginning before, instead of being taken as beginning at the end of, compression

in the machine. The combustible mixture is highly turbulent at the beginning of compression in the engine and is not so at any time in the single stroke machine.

Surface temperatures in the engine are less uniform than in the single stroke compression ignition machine mainly because the temperature of the necessary exhaust valve rises above that of other surfaces to an extent depending on the heat load which varies with M.S. and C.R., other conditions being unchanged. Thus the combustible mixture entering the engine is brought into contact with nonuniformly heated surfaces for the 360° of crank angle which may be taken as required for the induction and compression of the charge and represents a time of 0.15 sec. when the engine speed is 400 r.p.m. There is no induction stroke in the machine and surface temperature may be taken as uniform at the beginning of compression which, in the M.I.T. machine, generally occupied a time of 0.006 sec. and was therefore nearly adiabatic (7). An equal time of compression in the engine would require a speed of $400 \times \frac{0.075}{0.006} = 5000$ r.p.m. The delay period in

the M.I.T. machine, as in other compression ignition machines, is taken as beginning when compression is completed, that is, while the temperature and pressure of the reacting mixture are falling slowly from the maximum value attained. The delay period is therefore measured as if an engine running at 5000 r.p.m. were suddenly stopped at the finish of the compression stroke and held immobile until reaction starting in the compressed mixture did or did not lead to ignition. The delay period in an engine used as a compression ignition machine must be taken as ending prior to the completion of compression if combustion is to occur at nearly constant volume.

The characteristics of ignition by compression can be related to thermal efficiency and power when the engine is used as a compression ignition machine and by adjusting C.R. to an optimum value a rational basis is obtained for the relative tendencies of detonating fuels to autoignite when used at any particular M.S.

The single stroke machine as developed in the M.I.T. possesses the important feature that, after ignition occurs, the progress of the flame can be recorded photographically. The novel method of sealing the piston of the machine is effective and lubricating oil is not required. When the C.F.R. engine is used as a compression ignition machine, especially at the relatively low speed of 400 r.p.m., experimental difficulties arise from gas leakage at extremely high compression ratios and from the passage of lubricating oil into the combustion chamber. It was possible to obtain repeatable and significant experimental results solely by exercising the utmost care to keep the cylinder, piston, and rings in nearly new condition at the expense of much time and frequent replacement of parts.

Optimum C.R., Preignition, and Limit of Power Output, With Compression Ignition

The graphs of Figs. 1 and 2 illustrate the method used to determine Opt. C.R. and its variation with mixture strength. It had been assumed, prior to the

taking of indicator diagrams, that on adjusting C.R. to obtain maximum power output at a particular M.S., maximum combustion pressure would be attained at approximately 10° after t.d.c. The diagrams of Figs. 3 and 5 justify the assumption. Those of Fig. 3 show how the time of occurrence of maximum combustion pressure advances as C.R. is raised, and indicate accordingly that "preignition" may be defined as any igniting effect which causes maximum combustion pressure to occur earlier than 10° after t.d.c. *The extent to which this definition can be applied generally remains to be determined.*

The compression ignition experiments were carried out over the range of M.S. for which B.H.P. varied from zero to a maximum value. The graphs of Figs. 1 and 2 show that maximum power output was obtained with a M.S. approximately 10% rich when using heptane or hexane. Power output could not be increased by increasing either the M.S. or the C.R. An increase in either of these factors merely increased the rate of decomposition of fuel as was shown by an increase in carbon deposit in the combustion chamber and an increase in the density of black smoke in the exhaust.

The Delay Period With Ignition by Compression

The indicator diagrams of Fig. 3 are for a mixture 70% weak. They show that the beginning of the delay period advances and the length diminishes as C.R. is raised. It is difficult to determine the exact time of the beginning because it may not be accompanied by a pressure change other than that due in part to the increasing compression pressure. However, judged by pressure rises, it appeared to begin to approximately 10° before t.d.c., diagram No. 1, Fig. 3, and to advance by 3° only to 13° before t.d.c., diagram No. 4, the C.R. having been increased from 10 to 12.8. The length of the period, reckoned accordingly, decreased from 20° to only 4° . The rate of change diagram, Fig. 4, provides some further information in respect of the delay period. Thus the sudden increase in dp/dt at 8° before t.d.c. corresponds to the beginning of a first or preliminary stage of combustion as shown by diagram No. 2 of Fig. 3 but the preceding horizontal part of the diagram, Fig. 4, indicates that reaction began in the mixture at least 20° before t.d.c. Thus a determination of the length of the delay period, when using the engine as a compression ignition machine, presents some difficulty whereas it is a simple matter with the single stroke compression ignition machine if it is reckoned from the completion of compression. It is, however, shown very clearly by the engine experiments that the length of the delay period decreases as C.R. is raised, and it is of interest that a similar effect was shown by experiments with the M.I.T. single stroke machine, see conclusion No. 2 (8, p. 269).

Conclusion No. 1 of the reference quoted is that the "longest delays are observed at very lean or very rich mixtures". It is important to note that this conclusion is based on experiments made at constant C.R. with mixture strength varied and on reckoning the delay period as beginning on completion of compression. Engine experiments with constant compression ratio and variable M.S. were not made.

Conclusion No. 6 of the reference quoted is that "at very lean or very rich fuel ratios, the explosion is relatively mild". This conclusion is as in No. 1, based on experiments at constant C.R. However, referring to the graphs of Figs. 1 and 2, it will be seen that knock intensity in the engine diminished, from that observed at correct mixture, with decreasing concentration of fuel in the mixture with air. The engine experiments were made over a wider range of weak mixtures than that used for experiments with the M.I.T. machine and when using heptane for the engine experiments, Fig. 2, running was smooth and regular with a mixture 71% weak and combustion was inaudible at the Opt. C.R. of 11.7. Even on increasing C.R. to 14.1 to obtain sufficient preignition to reduce power output to zero, combustion knock was "light" only. There was always a considerable intensity of combustion knock when using rich mixtures but little increase as M.S. was increased and C.R. raised to maintain an optimum value. Thus it may be concluded that similar results were obtained by the engine and the M.I.T. machine although conditions were not quite comparable. The first part of conclusion No. 9 of the reference quoted above is that "the autoignition of *n*-heptane sometimes proceeds in two stages especially at lean fuel-air mixtures". The engine experiments exhibit a similar but more pronounced effect, thus the pressure-time indicator diagrams, Fig. 3, for mixtures 70% show two-stage ignition very clearly and the rate of change diagram, Fig. 4, shows the stages in quite a striking manner. Single-stage ignition only is shown by the pressure-time diagram, Fig. 5, for a nearly correct mixture. Thus results obtained with the engine are again in agreement with those obtained with the M.I.T. machine. The second part of conclusion No. 9 deals with the effect of tetraethyl lead (T.E.L.) on the delay period. Results of comparable engine experiments are not yet available.

The Relations Between Opt. C.R., M.S., Brake and Indicated Horsepower, and Brake and Indicated Thermal Efficiency

The method of determining the Opt. C.R. for any particular mixture strength as shown by the graphs of Figs. 1 and 2 was used to obtain the relation between Opt. C.R. and M.S. for mixtures with air of pentane, hexane, and heptane. Experimental results are given by the graphs of Fig. 6 for a charge density of 64% of normal and by those of Fig. 7 for a density of 78% of normal. The graphs are of a W form with two minimum values of Opt. C.R. and an intermediate maximum. Thus it is confirmed that when ignition is by compression, with the spark plugs replaced with blind plugs, the relation between Opt. C.R. and mixture strength for the three paraffins is similar to that obtained when acetaldehyde and diethyl ether were used as fuels in the same circumstances, see *B* graphs, Figs. 3 and 4, Part XIX (6).

The second minimum value of Opt. C.R. always occurred within the maximum power mixture strength range, namely, correct to 20% rich. The corresponding minimum value of the Opt. C.R. may therefore be taken as an approximation to the highest useful compression ratio (H.U.C.R.) in the conditions of the

experiments. The five fuels for which data are available from experiments at a particular charge density, namely 64% of normal, can then be rated as below:

	H.U.C.R.
Diethyl ether	4.8
Acetaldehyde	5.6
Heptane	8.3
Hexane	9.8
Pentane	10.0

Knock ratings can be determined in the conditions of the relatively high heat load of the C.F.R.-A.S.T.M. motor method of knock rating for the hexane and pentane only. The other fuels are not usable at maximum power M.S. in the temperature and charge density conditions, at compression ratios higher than the lower limit of the engine.

The relations between Opt. C.R., M.S., I.H.P., and B.H.P. are given by the graphs of Fig. 8; those between Opt. C.R., M.S., and indicated and brake thermal efficiency are given by the graphs of Fig. 9. The graphs are for the results of experiments with pentane-air mixtures. It will be noted that when C.R. was continuously adjusted to the optimum value, it was possible to continue reducing mixture strength until B.H.P. became zero. The mixture was then 75% weak. Similar experimental results were obtained when using mixtures of air with heptane or hexane. It is obvious from an inspection of the graphs and from the results of similar experiments with acetaldehyde and diethyl ether described in Part XX (3) that power and efficiency do not vary with compression ratio in the conventional manner, as mixture strength is reduced. This aspect of the experimental results involves consideration, as in Part XX (3), of the adverse effect on thermal efficiency due to the endothermic reaction required to produce nuclei of ignition and will be discussed, as mentioned earlier, together with the results of further experiments, in another Part.

The Igniting Effect of an Unfired Spark Plug

The results of experiments with acetaldehyde and diethyl ether, described in Part XIX (6) indicated that an igniting effect might be attributed to an unfired spark plug but relevant experiments were not made. The igniting effect again became apparent when paraffin fuels were used for the experiments of this Part and its magnitude and certain of its characteristics as determined by experiments with heptane and pentane made at 78% of normal charge density are exhibited by the graphs of Figs. 10 and 11. Thus it will be seen by reference to the graphs that the igniting effect became evident after M.S. had been increased to be greater than that corresponding to the first minimum value of Opt. C.R. When mixture strength was further increased to the correct value, the magnitude of the igniting effect was represented by decreases of 1.5 and 1.0 in the values of Opt. C.R. for mixtures with air of heptane and pentane, respectively.

The experimental results given by the graphs of Fig. 15 show that the igniting effect of the unfired spark plug must be attributed to the ceramic core, not to the

points. It may safely be assumed, however, that the core cannot have become hot enough in the low temperature conditions of the experiments to cause the direct surface ignition commonly described as preignition. Such an effect would not be subject to the precise control by C.R. over a wide range of M.S., shown by the graphs of Figs. 10 and 11 and by the results of other relevant experiments.

The igniting effect of the spark plug core is explicable by the nuclear ignition - pressure wave theory discussed in Part XX (3, p. 59). Thus compressed mixture in proximity to the core would attain a higher than average temperature and therefore be subject to preferential decomposition and consequent nuclear ignition. The explosive ignition of this relatively small part of the charge could initiate a pressure wave which on passing through the unburned part would complete decomposition progressively to the extent necessary to provide the concentration of nuclei required for its ignition.

When the unfired spark plug was replaced by a blind plug, it was necessary to raise the compression ratio in order to obtain ignition. The effect is shown by the graphs of Figs. 10 and 11 and is attributed to the relatively high surface temperature of the exhaust valve. That is, the exhaust valve, in the absence of the hotter spark plug core, may provide the heat required for the preferential decomposition and consequent nuclear ignition of adjacent mixture.

The Spark Ignition Delay Period

A carburetor type engine using ordinary liquid paraffinic fuels is operated in practice with ignition by spark and with the C.R. having a fixed value sufficiently low to avoid detonation. The temperatures and pressures attained prior to inflammation, even by the end gas, are then insufficient for the decomposition of the fuel, in the time available, to the extent necessary for nuclear ignition. In these circumstances a pressure rise due to combustion of the fuel does not occur until 10 to 12° of crank angle after passage of the spark and as mixture strength is reduced to become leaner than approximately 20% weak, rate of flame propagation becomes so low that combustion cannot be completed before expansion begins and may continue during the expansion and exhaust strokes. The consequences are that the exhaust valve may be damaged by overheating and the fresh charge ignited when the inlet valve opens. It is well known that these effects tend to occur in multicylinder engines because of uneven distribution of fuel. A single cylinder engine will cease to develop power before damage occurs.

It is important to remember that the experimental results given in this Part, except those shown by Figs. 1 to 3, are always for optimum values of C.R. and that it has been shown by indicator diagrams that maximum combustion pressure then occurs at approximately 10° after t.d.c. for any value of M.S.

Referring now to the experimental results for spark ignition, Fig. 12, it will be seen that when a correct mixture was used, it was necessary to raise Opt. C.R. from 5.45 to 6.25 on retarding the spark from 20° to 5° before t.d.c. When a mixture 20% weak was used, it was necessary to raise the Opt. C.R. from 6.05 to 8.1. When, however, a mixture 20% rich was used, it was necessary to

raise Opt. C.R. from 5.8 to 6.8. That is, in order that maximum combustion pressure would occur at 10° after t.d.c. when spark ignition was retarded from 20° to 5° before t.d.c., it was necessary to increase Opt. C.R. by 0.80 ratio at correct M.S., by 2.05 ratios at a M.S. 20% weak and by 1.0 ratio at a M.S. 20% rich. These results are in accordance with the view that as C.R. is raised to maintain an optimum value as spark timing is retarded, the necessary increase in rate of flame propagation is due to an increase in the concentration of nuclear centers of ignition. The smaller increase of Opt. C.R. required for rich as compared with weak mixtures is attributed to the concentration of nuclei increasing with increase of mixture strength but secondary effects must be taken into account. Thus the heat load which affects the velocity of the decomposition reaction has a maximum value at correct mixture strength, approximately. The heat load diminishes on the weak side of correct M.S. with the decrease in the concentration of fuel in the mixture with air but it also diminishes on the rich side as the concentration of fuel in the mixture *increases* because of the consequent imperfect combustion and the reduction of temperature which always accompanies the use of overrich mixtures. Moreover this reduction of temperature may be due in part to the heat absorbed by the endothermic decomposition reaction which in the circumstances results in the profuse formation of carbon.

It is significant that as spark ignition is retarded, the graphs for the relation between Opt. C.R. and M.S. tend to assume the W form shown by the broken line graphs of Fig. 12 which were obtained when ignition was by compression at the relatively high values of Opt. C.R. required for decomposition of the fuel to the extent required for nuclear ignition.

CONCLUDING NOTES

The experiments described in this Part indicate the extent to which important characteristics of ignition and combustion can be investigated when the C.F.R. engine is used as a compression ignition machine. The results show that further experimental work would be profitable in respect of the following:—

- (1) The nature of the nuclei formed by decomposition of the fuel, especially when very lean mixtures are used.
- (2) The effect of decomposition reactions on thermal efficiency when knock resistant liquid hydrocarbon fuels are used.
- (3) The temperatures of indirectly cooled surfaces such as exhaust valves and spark plug cores, as affected by heat load.
- (4) The temperatures of the indirectly cooled surfaces that are required for ignition of the fuel-air mixture by direct contact and the nature of the products then formed by surface reactions.
- (5) The temperatures of the indirectly cooled surfaces which are required for the initiation of a pressure wave in a mixture already sensitized to ignition by the products of a decomposition reaction and the rate of flame propagation in such a mixture.

(6) The inability of the electric spark to ignite mixtures leaner than approximately 45% weak as compared with the extension of an igniting effect to mixtures even leaner than 90% weak by compression ignition when fuels subject to nuclear ignition are used.

(7) The effect of heat load to limit the compression ratio usable with non-detonating fuels such as hydrogen, natural gas (methane), and manufactured gas.

Every item listed above can be regarded as a particular research project and the number could easily be increased. An investigation of even the items enumerated would be of interest concerning the mechanism of ignition and combustion in Diesel as well as in spark ignition engines and would probably add to present knowledge of the cause of explosions of combustible dusts and of the conditions required for the exceptionally rapid combustion of fuel air mixtures in other than piston engines.

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**THE OXIDATION, DECOMPOSITION, IGNITION, AND
DETONATION OF FUEL VAPORS AND GASES**

**XXII. THE CHARACTERISTICS OF THE IGNITION AND COMBUSTION OF
BENZENE IN A CARBURETOR ENGINE AS AFFECTED BY HEAT LOAD**

BY R. O. KING AND A. B. ALLAN

THE OXIDATION, DECOMPOSITION, IGNITION, AND DETONATION OF FUEL VAPORS AND GASES

XXII. THE CHARACTERISTICS OF THE IGNITION AND COMBUSTION OF BENZENE IN A CARBURETOR ENGINE AS AFFECTED BY HEAT LOAD¹

By R. O. KING² AND A. B. ALLAN³

ABSTRACT

The object of the experiments was to determine the effect of "heat load" on the combustion and ignition characteristics and the relation between thermal efficiency and compression ratio as mixture strength was varied, when using a fuel such as benzene which does not decompose in carburetor engines operated in normal conditions, in a manner to provide nuclei required for autoignition. Experiments were made first in the conditions of the low heat load resulting from the use of a subnormal charge density, an engine speed of 400 r.p.m., the jacket coolant at 100°F., and the air supply at 50°F. In these circumstances it had been possible in earlier experiments, at suitable values of compression ratio, to use nuclear instead of spark ignition if the fuels were normal varieties of heptane, hexane, or pentane; but when using the same conditions for the experiments of this Part, benzene always required spark ignition and burned so slowly that spark timing could not be adjusted to ensure that the heat of combustion was added to the working fluid at even approximately constant volume, and it was possible by suitable adjustment of spark timing and compression ratio to obtain a constant pressure cycle. Preignition did not occur, even when using a hot spark plug and compression ratios rising to 15:1. A series of experiments was then carried out in conditions of the normal heat load resulting from the use of full charge density, an engine speed of 900 r.p.m., the jacket coolant and the air supply at 140°F. It was then possible to run the engine on a nearly constant volume cycle with a consequent increase in thermal efficiency. Two medium temperature spark plugs were used and indications of impending preignition occurred at a compression ratio of 14:1. The I.M.E.P. had then attained a maximum of 153.2 lb. per sq. in. when the mixture was 20% rich. Spark ignition was still required for continuous running. On changing to a "hot" variety of spark plug, severe preignition accompanied by heavy pounding occurred. The timing of the effect advanced so rapidly that power output fell to zero in approximately 40 sec.; an effect which is illustrated by indicator diagrams taken at 10-sec. intervals. The characteristics of the combustion and ignition of benzene in the C.F.R. engine are shown to depend fundamentally on heat load and the experimental results are discussed accordingly in a final section of text.

INTRODUCTION

Experimental results obtained when using benzene as a fuel for the C.F.R. engine in conditions required for a low heat load are given in Section (1).

Results of experiments made in normal heat load conditions are given in Section (2). There was a tendency to preignition of the benzene-air mixtures in these conditions. This was found to depend on the heat rating of the spark plugs and experiments made accordingly are described in Section (3).

The characteristics of ignition and combustion of the benzene-air mixture as affected by heat load are discussed in Section (4).

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EXPERIMENTAL METHODS

The experiments were carried out with the C.F.R.-F.2 engine and auxiliary equipment, as used for the experiments with normal paraffins (4). Thus, the C.F.R. shrouded inlet valve was replaced by one of the ordinary tulip-shaped variety; the carburetor was bolted directly to the engine head after removal of the C.F.R. mixture heater; the air supply was cooled to nearly 0°F. to remove excess moisture and then heated to the temperature required. The temperature of the jacket cooling water was controlled by the thermostatic method described in the appendix to Part XIII (5). The difference between the inlet and outlet temperatures was never more than 5°F. The outlet temperature only will be stated in subsequent text as that of the jacket coolant.

The engine cylinder used for the experiments was in nearly new condition. The bore had less than 0.003 in. taper and the surface was clean and unscored. After a new piston and rings and a new wrist pin had been fitted, the engine was "run in" carefully before beginning the experiments.

The cylinder was of the "four hole" type, that is holes were provided for three spark plugs in the wall of the combustion chamber in addition to the bouncing pin hole in the cylinder head. The bouncing pin was not used. It was replaced by a mild steel plug when ignition was by a single spark plug and by a spark plug when two spark plugs were used.

Benzene of the A.S.T.M. "Nitration" grade, as supplied by the Steel Company of Canada, was used for the experiments. It was colorless and free of CS_2 or H_2S . The boiling range did not exceed 1°C. and included the value of 80.1°C. of the pure substance. Thermal efficiencies given in the test are based on the lower calorific value being 17,261 B.t.u. per lb.

A commercial variety of S.A.E. 10, Pennsylvania lubricating oil, without additives was used for all of the experiments. It was maintained at 120°F. in the sump.

Characteristics of combustion in the engine are illustrated by diagrams taken with a Sunbury electronic indicator with which is used a variable magnetic flux pressure pickup. The steel diaphragm which is exposed to the pressure in the cylinder, the permanent magnet, and the search coil of the pickup are contained within a steel shell which can replace an 18 mm. spark plug. The diagrams as shown by the cathode ray oscillograph were photographed by a Leica camera. A notched timing wheel mounted on the out-board end of the dynamometer shaft was used to provide "blips" on the time scale of the diagrams. The blips were arranged to occur when the piston was at top dead center (t.d.c.) and at 10 degree intervals for 30 degrees before and after. Short vertical lines have been added to the diagrams for extra convenience of marking the t.d.c. piston position. The somewhat irregular spacing of the blips is due in part to there being some degree of elasticity between the piston and the timing wheel, but mainly to the inertia of rotating parts being insufficient to prevent the cyclic pressure changes in the cylinder causing similar changes in the speed of rotation of the timing wheel.

Diagrams are given both for the variation of pressure with time and the variation of rate of change of pressure with time. The horizontal lines of the diagrams correspond with the parts of the induction and exhaust strokes for which there are no appreciable pressure changes. The rate of pressure change passes through a zero value when the pressure of combustion attains a maximum and the corresponding piston position is shown by the point on the diagram at which positive values for rate of change become negative.

The terms compression ratio, optimum compression ratio, and mixture strength are abbreviated in subsequent text to C.R., Opt. C.R., and M.S. respectively. Stoichiometric mixtures of benzene and air are described as "correct."

SECTION (1). EXPERIMENTS WITH A COOL ENGINE

Low Heat Load

The running conditions were as used earlier for the experiments with the normal paraffins, Part XXI (4). They were: an engine speed of 400 r.p.m., a jacket coolant (water) temperature of 100°F., an air supply temperature of 50°F., and a charge density of 64% of normal. One spark plug only was used, a Champion C.F.R.-8, described as a "hot" variety, near the top of a commercial heat scale. It was set in the standard position in the wall of the combustion chamber midway between the exhaust and inlet valves.

Method of Determination of Opt. C.R.

The rate of burning, after spark ignition, of the normal paraffins was controllable by pressure; thus, at particular values of mixture strength and spark advance, the position of maximum combustion pressure relative to t.d.c. could be advanced or retarded on raising or lowering the compression ratio. The rate of burning of *benzene* after spark ignition appeared to vary little with change of pressure, in the conditions of the experiments. The small increase observed on increasing the compression ratio could be attributed to the corresponding increase of temperature. This characteristic of benzene is illustrated by the two indicator diagrams of Fig. 1, taken when using a

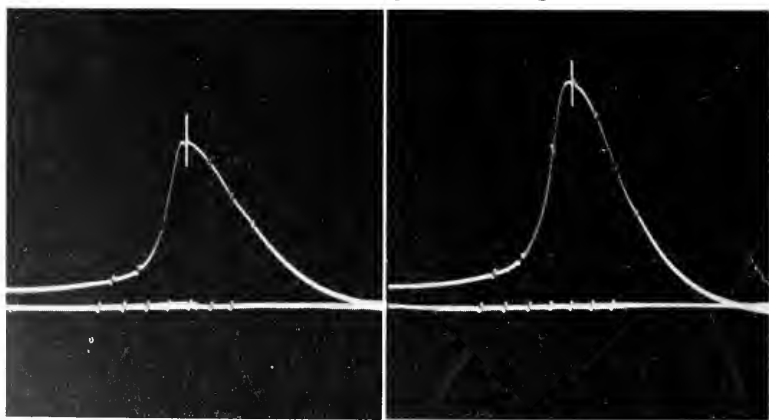


FIG. 1. Pressure-time diagrams taken at compression ratios of 7.42 and 9.39. Spark 30° before t.d.c., correct mixtures, cool engine.

correct mixture with air, at compression ratios of 7.42 and 9.39, and with spark ignition 30° before t.d.c. The diagrams show that the increase of combustion pressure due to the increase of C.R. occurred in large part before t.d.c. The consequent increases in L.H.P. and I.T.E. were 1.0% and 1.35% respectively while B.H.P. *diminished* from 1.09% to 1.07.

The two diagrams are from a series of five taken to determine the C.R. required for maximum thermal efficiency when using a correct mixture and 30° spark advance, that is the optimum value of C.R. in the conditions of the experiments. The method adopted to obtain a true value of the Opt. C.R. corresponding to a particular combination of spark advance and mixture strength is illustrated by the data given in Table I, as obtained in the course of taking the series of five diagrams.

TABLE I
DATA REQUIRED FOR A DETERMINATION OF OPT. C.R.,
CORRECT BENZENE-AIR MIXTURE, 30° SPARK ADVANCE

C.R.	B.H.P.	L.H.P.	I.H.P.	I.T.E., %
7.42	1.093	0.411	1.534	25.8
7.91	1.093	0.453	1.546	26.0
8.41	1.087	0.465	1.552	26.1
8.91	1.090	0.478	1.568	26.1
9.39	1.070	0.487	1.557	26.2

The remarkably small change in B.H.P. due to increasing C.R. from 7.42 to 9.39 is shown by Column 2 of the table; it will be noticed that values of B.H.P. *decreased* as C.R. was raised. This anomalous result is attributed to the increase in the rate of burning of the benzene due to the increase in charge temperature obtained by raising the Opt. C.R. from 7.42 to 9.39. Thus spark advance having remained at 30°, maximum combustion pressure occurred farther in advance of t.d.c. than when C.R. was 7.42.

The power required to overcome friction and pumping losses (L.H.P.) was measured with great care in the course of the experiments. It increased quite consistently as C.R. was raised from 7.42 to 9.39. On taking the sum of B.H.P. and L.H.P. to obtain I.H.P., the data in Columns 4 and 5 of the table were obtained. It will be noted that small but definite maximum values for I.H.P. and the corresponding I.T.E. were obtained for a C.R. of 8.91. This C.R. may therefore be taken as the optimum value. Thus were determined all of the values for Opt. C.R. given in this section. Samples of the graphs required for determinations of Opt. C.R. are given in Fig. 2.

Cool Engine Performance at Opt. C.R. as Affected by Ignition Timing: Constant Volume and Constant Pressure Cycles

Optimum performance in terms of power and thermal efficiency would not be expected from benzene when it was used in the cool engine and with spark advance 30° before t.d.c. because a maximum value of the pressure due to combustion occurred slightly before t.d.c. The power output in the circumstances was due to the benzene continuing to burn after the piston had

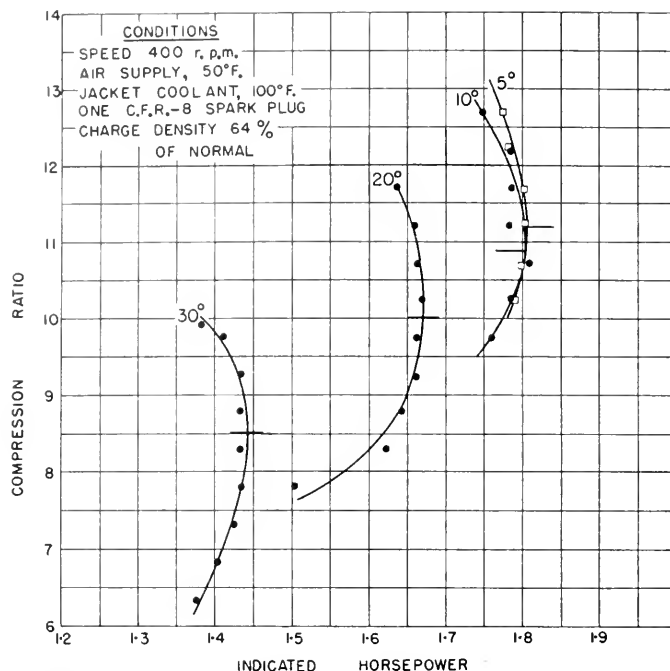


FIG. 2. Graphs for the relation between C.R. and I.H.P., as used for the determination of Opt. C.R., corresponding to spark advances of 5, 10, 20, and 30° before t.d.c., cool engine.

passed t.d.c. as shown by the form of the maximum pressure part of the diagrams of Fig. 1.

The rate of burning of benzene being largely independent of pressure, the effective method of retarding maximum combustion pressure to occur after t.d.c., while maintaining a correct mixture, would be to delay ignition. Results obtained accordingly with ignition advances of 20° and 10° are illustrated by the indicator diagrams of Fig. 3. Related data are set out in Table II, together with similar data from Table I obtained with a spark advance of 30°.

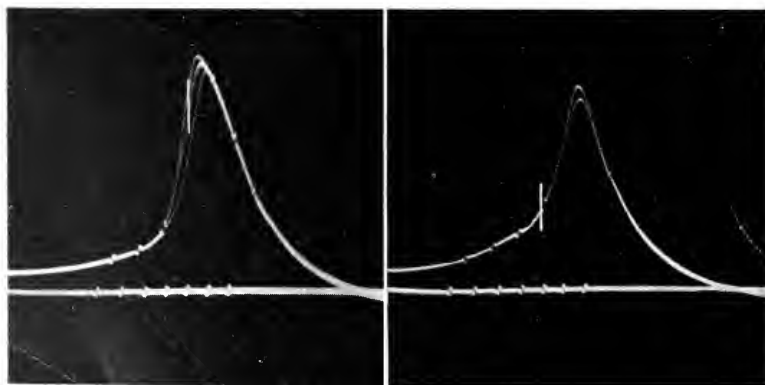


FIG. 3. Pressure-time diagrams showing the retardation of maximum combustion pressure from 5 to 15° after t.d.c. as spark is retarded from 20 to 10° before t.d.c. Opt. C.R. increasing from 9.88 to 11.38, correct mixtures, cool engine.

TABLE II
EFFECT OF IGNITION TIMING ON PERFORMANCE,
CORRECT BENZENE-AIR MIXTURES, COOL ENGINE

Spark advance	Time of max. comb. press.	Opt.C.R.	I.H.P.	I.T.E.
30°	2° before t.d.c.	8.91	1.568	26.4
20°	5° after t.d.c.	9.88	1.785	30.0
10°	15° after t.d.c.	11.38	1.911	32.6

The data, Table II, show the improvement in performance in terms of I.H.P. and I.T.E. obtained as the occurrence of maximum combustion pressure was retarded from 2° before to 15° after t.d.c., on retarding the spark from 30° to 10° before t.d.c. The improvement in performance was, however, obtained at the expense of increasing Opt. C.R. from 8.91 to 11.38.

The engine tended to run on a constant pressure cycle as spark advance was further retarded and C.R. increased. Thus on retarding the spark to occur at t.d.c. and using a mixture 15.5% weak, a striking example of constant pressure cycle running was obtained. The pressure-time and rate of change diagrams then taken are exhibited by Fig. 4. The Opt. C.R. was 14.9. It will

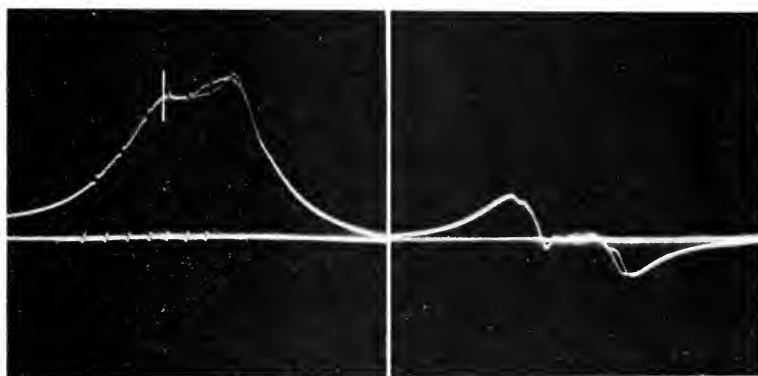


FIG. 4. Pressure-time and rate of change diagrams showing a constant pressure cycle. Spark at t.d.c. and mixture 15.5% weak. C.R. 14.88, cool engine.

be seen by reference to the diagrams that combustion pressure began to increase immediately after spark ignition, but slowly, to a maximum at 30° after t.d.c. The rate of change diagram shows little change of pressure during the period. The two diagrams were of course not taken simultaneously and cycles did not repeat exactly in the conditions of the experiments. The I.T.E. was 32.2%, which is not a high value for a C.R. of 14.9. The diagrams provide a good picture of combustion as it might occur in a slow running Diesel with the fuel injected by a high-pressure air blast at the end of compression. The broken line diagram of Fig. 5 is for compression and expansion of air only. It was taken at the time of the experiments but at the slightly higher C.R. of 15.3. The difference between diagrams A and C provides an additional

illustration of the constant pressure nature of the cycle. Diagrams A and C were superimposed after being drawn from enlargements of original Leica negatives and then rephotographed.

It was necessary that combustion of the benzene should occur at constant volume if experimental results were to be comparable with those obtained when using the normal paraffins. The experimental results obtained with a

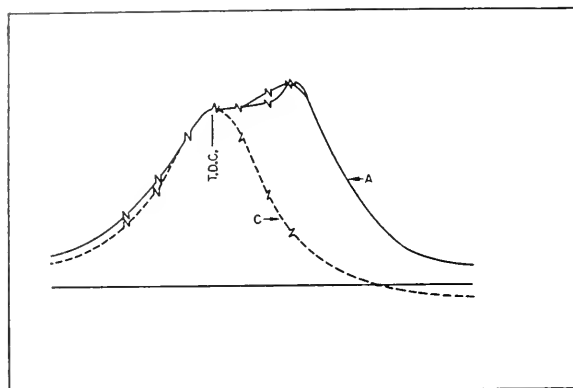


FIG. 5. Pressure-time diagram of Fig. 4 compared with one taken for the compression and expansion of air only.

spark advance of 10° or less would therefore not be suitable. Moreover it would have been necessary, even with a spark advance of 10° , to do the experiments at values of Opt. C.R. higher than the 11.38 determined for a correct mixture when weaker or richer mixtures were used. The engine performance in these circumstances would again not be comparable with that obtained for the normal paraffins at values of C.R. ranging from 8 to 10 for mixtures ranging from 40% weak to 20% rich and with ignition by compression.

It has been shown, Table II, that 30° spark advance is unsuitable in that maximum combustion pressure then occurs before t.d.c. and it was concluded that optimum performance in the cool conditions of running would be obtained over a wide range of M.S. by using a spark advance of 20° . Indicator diagrams were taken accordingly with mixtures ranging from 37.7% weak to 47% rich, C.R. being always adjusted to the optimum value. Data from the diagrams are tabulated below.

The data of Table III obtained with ignition fixed at 20° advance indicate that as Opt. C.R. is increased on going from correct to weaker or richer mixtures, the corresponding increase in compression temperature leads to increases in the rate of burning of the benzene which tend to compensate for the decrease which would occur if C.R. and the corresponding temperature attained by compression remained constant. Thus was obtained the nearest approach to a constant volume cycle that was possible over a wide range of mixture strength in the cool running conditions in which benzene burns at a relatively low rate.

TABLE III

EFFECT OF CHANGE OF MIXTURE STRENGTH ON TIME OF OCCURRENCE OF MAXIMUM COMBUSTION PRESSURE, COOL ENGINE 64% OF NORMAL CHARGE DENSITY, 20° SPARK ADVANCE

Mixture strength	Opt. C.R.	Max. comb. press.
37.7% weak	11.8	9.10 after t.d.c.
23.3% "	10.9	12 " "
15.5% "	10.3	9 " "
5.1% "	10.1	7.8 " "
Correct	9.9	6.7 " "
8.8% rich	10.3	7 " "
28.2% "	10.3	7 " "
47.0% "	11.3	8 " "

Cool Engine Performance with Spark Timing Fixed at 20° Advance

The performance of the engine in terms of indicated and brake horsepowers and corresponding indicated and brake thermal efficiencies is given by the graphs of Fig. 6. Spark timing was fixed at 20° advance and C.R. was always adjusted to an optimum value which increased from 10.0 to 14.9 as M.S. was reduced from correct to 39% weak; indicated thermal efficiency then attained a maximum value of 35%.

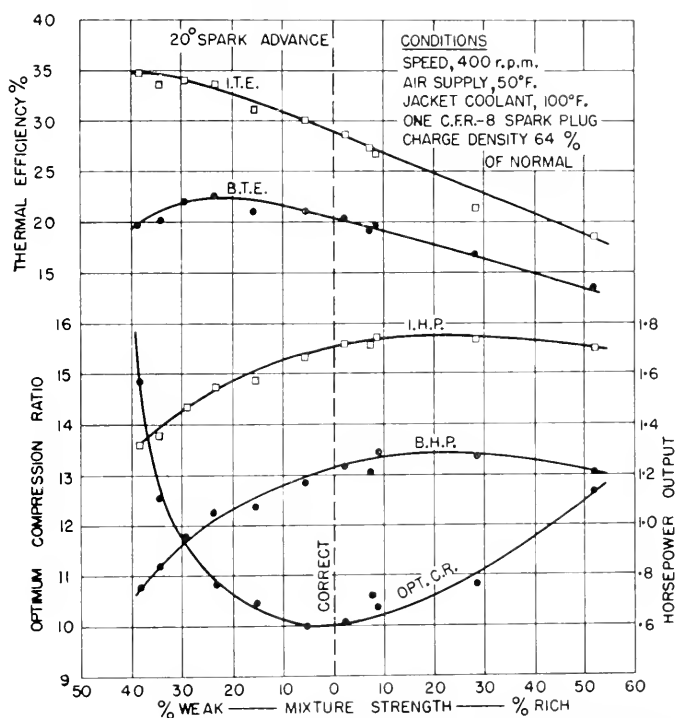


FIG. 6. Graphs showing performance of cool engine in terms of thermal efficiency and power output with spark fixed at 20° before t.d.c. Mixtures varying from 40% weak to 50% rich and C.R. always adjusted to the optimum value.

Maximum values of I.H.P. and B.H.P. were attained when using mixtures 20% rich. The I.M.E.P. was then 94 lb. per sq. in. and the indicated thermal efficiency 25%.

The object of the experiments was to obtain the relation between indicated thermal efficiency and Opt. C.R. for mixtures varying from rich to the leanest practicable. This relation is shown by the graph of Fig. 7 for mixtures varying from 10% rich to 39% weak. This graph was plotted from the data given by the graphs of Fig. 6.

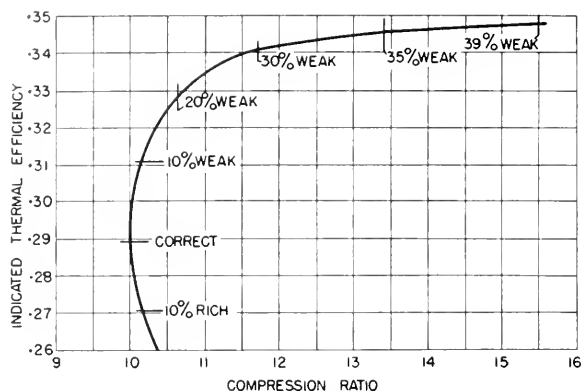


FIG. 7. Graph showing the relation between indicated thermal efficiency and C.R. as mixture strength is reduced from 10% rich to 39% weak. Spark fixed at 20° before t.d.c., cool engine.

The inferior performance of the engine is attributed fundamentally to the slow burning characteristic of benzene in the cool running conditions with a subnormal charge density.

SECTION (2). EXPERIMENTS WITH A HOT ENGINE

Normal Heat Load

It was shown by the experiments of Section (1) made with a cool engine, see graphs of Figs. 6 and 7, that I.T.E. increased from 34.2 to 34.8 only on raising the C.R. from 12.0 to 15.5 while decreasing the M.S. from 31 to 39% weak. This characteristic is not as would be expected. There was a possibility that it could be attributed to the low temperature running conditions and the subnormal charge density used for the experiments. The engine tended to operate on a constant pressure cycle in these conditions, in which the combustion of benzene occurred at a relatively low rate. It was decided therefore to determine the relation between I.T.E. and C.R. with diminishing M.S., in normal running conditions. These ensured a relatively hot engine.

The change from a cool to a hot engine was made by altering running conditions as follows:

The speed was increased from 400 to 900 r.p.m., which had been found to be the optimum for the valve timing of the C.F.R. engine as used for the knock rating of motor fuels. The jacket coolant temperature was raised from

100°F. to 140°F. outlet temperature. The temperature of the air supplied to the carburetor was raised from 50 to 110°F. The electric air heater then consumed approximately 250 watts. The carburetor choke tube used to obtain the subnormal charge density of the cool engine experiments was replaced by the standard C.F.R. carburetor venturi with a throat diameter of 9/16 in. to obtain normal charge density.

Benzene became liable to preignition by a hot spark plug in the changed running conditions, and the Champion, 18 mm. C.F.R.-8 hot plug in the standard position was replaced by a cooler plug, Autolite B.T.1. A second spark plug was used diametrically opposite, in the bouncing pin position. This was an Autolite T.T.1. It was of the same heat rating as the B.T.1 but was obtainable in the 7/8 in. size as required to fit the bouncing pin hole.

The Relation Between I.T.E., C.R., and Spark Advance

It was found, on beginning experiments with the hot engine, operated at normal charge density and at 900 r.p.m., that if spark advance were treated as a variable factor and C.R. and M.S. maintained at fixed values, it was easily possible to determine the optimum combination of the three factors, that is, the combination at which a maximum value was obtained for I.T.P. Typical examples of the method are given by the graphs of Fig. 8 for three

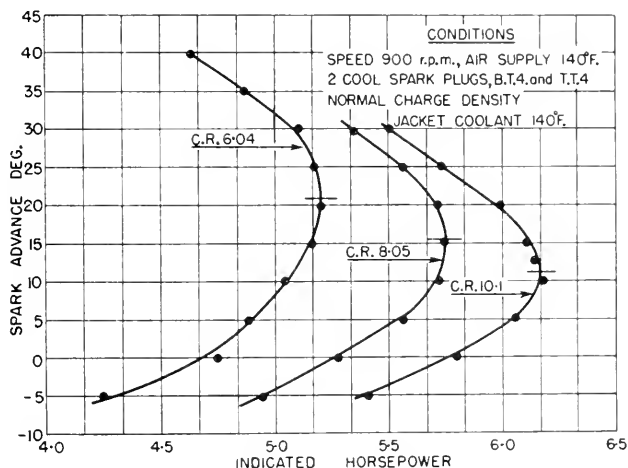


FIG. 8. Example of the method of determining optimum spark timing for particular values of C.R., mixture being always 8% weak. Hot engine.

particular values of C.R. with M.S. always 8.0% weak. It will be seen by reference to these graphs that the spark advances required for maximum I.T.E., as shown by the short horizontal lines, could be determined with a fair degree of accuracy.

The results obtained by using the method at a fixed C.R. of 8.0 and at eight particular values of mixture strength from 43% weak to 11% rich are

given by the graphs of Fig. 9. It is to be understood that optimum spark advance having always been determined, then at any M.S. the value given for I.T.E. corresponds with the C.R. of 8.0 being an optimum value.

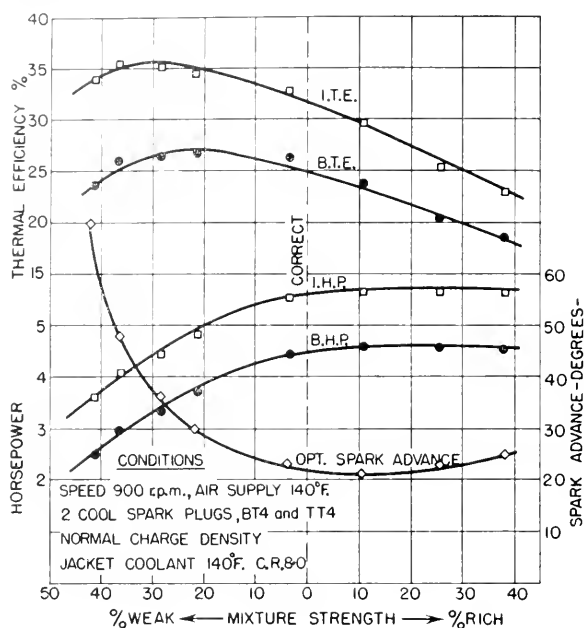


FIG. 9. Graphs showing hot engine performance in terms of power and thermal efficiency, mixtures varying from 40% weak to 40% rich. C.R. 8.0, optimum spark timing.

The Relation between I.T.E. and M.S. for Optimum Values of C.R. Ranging from 4 to 13

The primary object of the experiments was to obtain a relation between I.T.E. and C.R. as mixture strength was diminished, comparable with that obtained when using the cool engine, Section (1). It was necessary, accordingly, to carry out experiments at values of C.R. of 10 and higher because it will be seen by reference to Figs. 6 and 7 that, with the cool engine and a fixed spark advance of 20°, optimum values of C.R. were never less than 10.

Experiments by others, with benzene-air mixtures, to determine the relation between I.T.E. and C.R. have always been made, so far as known, with values of C.R. less than 10 and with particular values of M.S. Pye, for example (6, p. 181), describes experiments, evidently made by Ricardo with the E.35 engine, over a C.R. range of from 4 to 6.9 only. Preignition occurred at the higher value of C.R. and the experiment was discontinued (7, p. 144). A C.R. of 8.0 was the mechanical limit of the E.35 engine.

It was considered therefore that in addition to obtaining the data for a C.R. of 8.0 as given by the graphs of Fig. 9 and as required for the higher values of C.R. used for the cool engine experiment of Section (1), it would be of general interest to extend the experimental work to obtain similar data for values of C.R. ranging from 4 to 8.

Experiments were carried out accordingly, beginning with a C.R. of 1.0 and with higher values rising by steps of 1 to the practicable maximum of 13.0. Complete data as given by the graphs of Fig. 9 were obtained for the 10 particular values of C.R. but data relating only to the variation of I.T.E. with C.R. and M.S. are given, see Fig. 10.

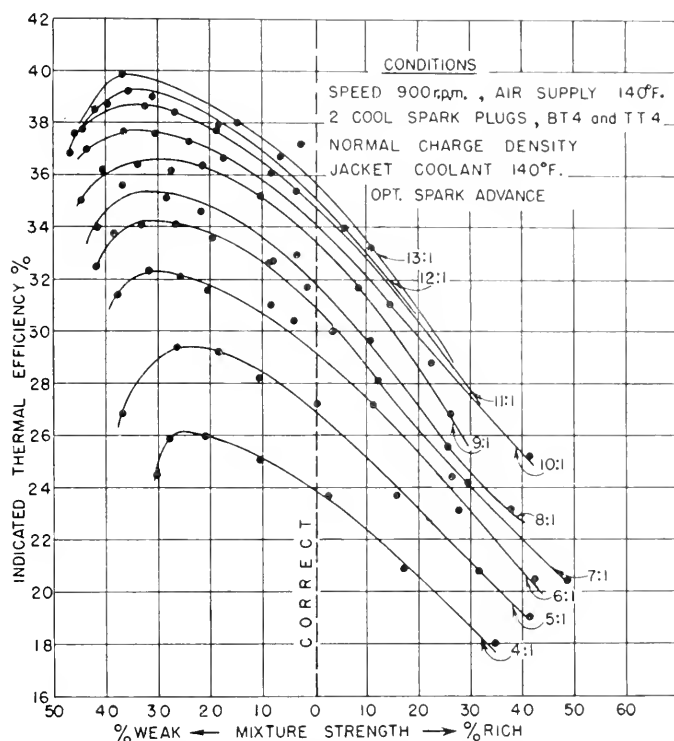


FIG. 10. Family of graphs for relation between indicated thermal efficiency and mixture strength, for values of C.R. of from 4 to 13:1, spark timing always adjusted to an optimum value. Hot engine.

It will be seen by reference to the figure that

(1) The M.S. for which I.T.E. is a maximum moved continuously to weaker mixtures as C.R. was raised. Thus at a C.R. of 4.0 a maximum I.T.E. of 26.1% was obtained for a mixture 26% weak, but at a C.R. of 13.0 a maximum I.T.E. of 39% was obtained for a mixture 37% weak. It will be noted also that the value of the weakest usable M.S. moved from 30% weak at a C.R. of 4.0 to one of 45% weak at a C.R. of 13.0.

(2) Graphs relating I.T.E. to values of Opt. C.R. ranging from 1.0 to 13.0 cannot be drawn for mixtures leaner than 20% weak. At 30% weak they can be drawn for values of Opt. C.R. ranging from 5 to 13 and at 10% weak for values of Opt. C.R. ranging from 8.0 to 13.0; at weaker mixtures ignition became irregular even at values of Opt. C.R. higher than 8 unless spark plugs of a higher heat rating were used.

(3) The most immediately useful data obtained from the graphs of Fig. 10 are those which enable a graph, comparable with that of Fig. 7 for the cool engine experiments, to be shown for the hot engine experiments. The two graphs are exhibited by Fig. 11. Referring to the lower graph, it will be seen that at a C.R. of 11.7, the I.T.E. for a mixture 30% weak is 34.1%.

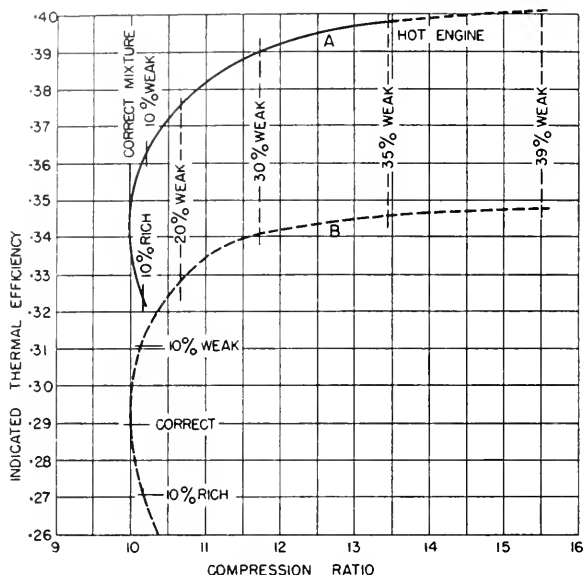


FIG. 11. Graph A shows the relation between indicated thermal efficiency and C.R. as mixture strength is reduced from 10% rich to 39% weak. Optimum spark timing, hot engine.

Graph B, broken line, is a reproduction of the graph of Fig. 7 for cool engine with spark timing fixed at 20° before t.d.c. and C.R. always adjusted to an optimum value.

Now, referring to the graphs of Fig. 10, it will be seen that the I.T.E. for a mixture 30% weak is 38.8% at a C.R. of 11.0 and 39.2% at a C.R. of 12.0. By interpolation the I.T.E. is therefore 39.1% for the 30% weak mixture at a C.R. of 11.7. This process illustrates how the upper graph is obtained. The upper and lower graphs are thus strictly comparable and show an average difference of 5.3% in I.T.E. for all values of C.R. and mixture strength. The difference is in favor of the hot engine and at correct mixtures and 10.0 C.R. represents an increase of approximately 19% in I.T.E.

An adequate explanation for the higher values of I.T.E. obtained with the hot engine is provided by a consideration of the piston positions at which combustion of the benzene occurred.

Maximum power was obtained with the cool engine when maximum combustion pressure occurred at from 6 to 9° after t.d.c. with values of M.S. varying from 37% weak to 47% rich, see Table III. This, in view of the slow burning of benzene in the cool engine, meant that a considerable part of the pressure rise due to combustion had occurred before t.d.c. with the effect of reducing power and thermal efficiency.

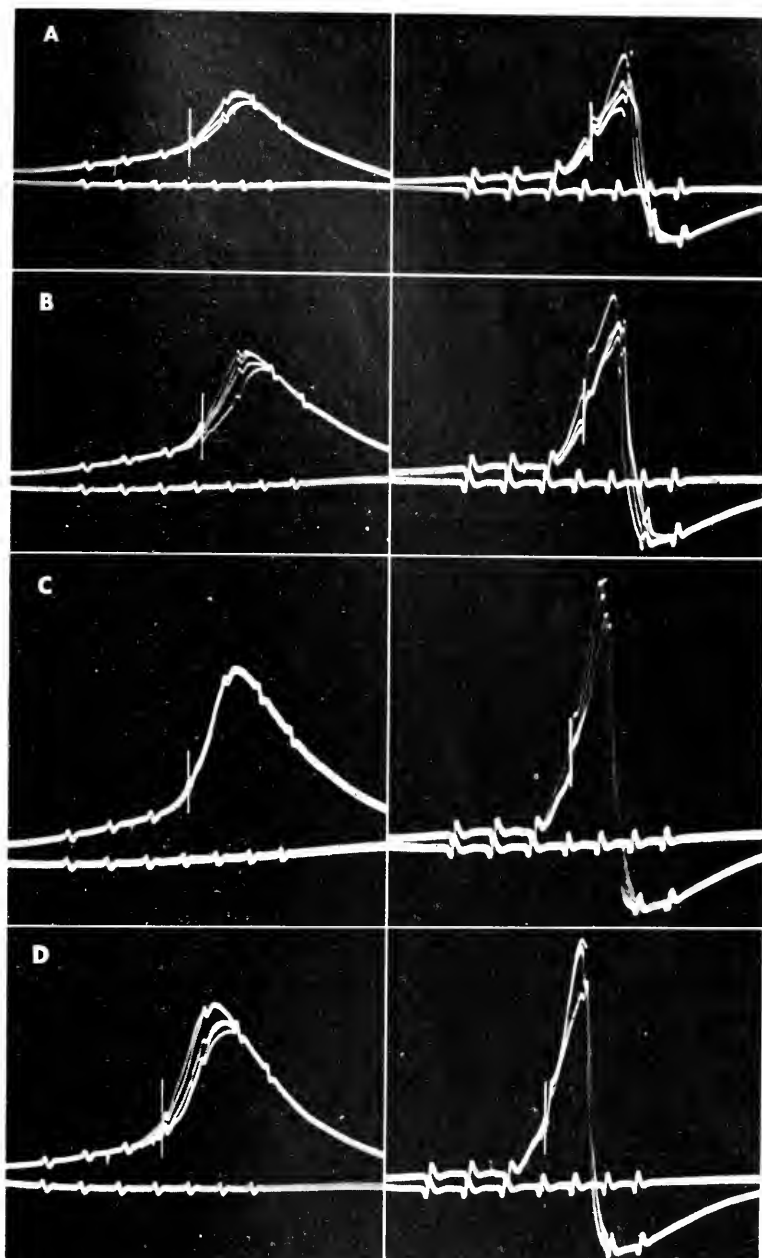


FIG. 12. Pressure-time and rate of change diagrams for mixtures ranging from 25.7% weak to 24.6% rich. C.R. 8:1, hot engine. The diagrams show the relation between optimum spark timing and the time of occurrence of maximum combustion pressure. Note, spark timing is recorded electronically by the single downward blips on the pressure-time diagrams.

- | | | | | | | | | |
|----|---------|------------------|-----------|-----|--------|------|--------|-------|
| a. | Mixture | 26% weak | spk. adv. | 21° | I.H.P. | 1.56 | I.T.E. | 34% |
| b. | " | 8.6% | " | " | 15° | " | 5.24 | " 32% |
| c. | " | 3.0% rich | " | " | 13° | " | 5.76 | " 32% |
| d. | " | 24.6% | " | " | 13° | " | 5.69 | " 26% |

The benzene burned more rapidly in the temperature conditions of the hot engine, and when spark advance was adjusted for maximum power, the pressure rise due to combustion occurred mainly after t.d.c. with a maximum at from 12 to 16° after that piston position, depending on M.S. These characteristics of the combustion of benzene in the hot engine are illustrated by the series of pressure-time and rate of change diagrams, Fig. 12, taken at a C.R. of 8.0. Data from the diagrams are tabulated below.

TABLE IV

Mixture	Opt. spark advance	Max. comb. press.
26% weak	21°	16° after t.d.c.
8% weak	15°	12° after t.d.c.
3% rich	13°	12° after t.d.c.
25% rich	13°	13° after t.d.c.

SECTION (3). IGNITION BY HOT SURFACES; PREIGNITION

Ignition of the charge by an overheated surface in the combustion chamber of a spark ignition engine is commonly described as "preignition", irrespective of time of occurrence. The timing of the igniting effect may coincide with that of spark timing. In that case the engine will continue to run steadily with the spark switched off if load, mixture strength, and the temperature of the hot surface remain constant. If however spark timing has been adjusted for maximum power and ignition by a hot surface occurs later, then if the spark is switched off, the engine may continue to run but maximum power will not be developed. The temperature of the hot surface will diminish accordingly and progressively until the igniting effect ceases and the engine stops running, with no harm done.

If spark ignition timing has been adjusted for maximum power output and ignition by a hot surface then occurs earlier, it is described correctly as *preignition*. The immediate consequence of the effect is the liberation before t.d.c. of an increased proportion of the heat of combustion. The temperature of the hot surface and the timing of its igniting effect will then increase progressively until ignition occurs so early in the compression stroke that a single cylinder engine ceases to develop power. If, however, preignition occurs in a particular cylinder of a multicylinder engine which continues to run, severe damage will occur in the affected cylinder, especially if the engine be supercharged. The damage has been described by others, notably by Hundere and Bert (1).

Ignition by a hot surface, which occurs later than spark ignition, is described by Hundere and Bert as "after-ignition". It is an apt term but, in order to make a correct distinction between preignition and after-ignition, it is necessary to establish a timing datum. That can be taken as the spark timing required for maximum power output and it is obvious that it will

vary with C.R., M.S., and charge density. Suppose, for example, that spark timing be set too late for maximum power output and that surface ignition occurs earlier, the ignition would not be preignition according to the definition and provided its timing did not advance progressively a beneficial effect on performance would be obtained.

The spark plug if of a "hot" variety generally provides the surface of maximum temperature in the combustion chamber of an engine. A consequent igniting effect was found in earlier experiments to be due to the ceramic core, not to the electrodes (1, p. 239). Such an igniting effect did not occur when the benzene-air mixtures were used in the cool engine, Section (1), even when using a hot spark plug, C.F.R.-8, and values of C.R. rising to 15.0. When, however, the mixtures were used in the hot engine run at 900 r.p.m. and with normal charge density, indications of "after-ignition" were observed at values of the C.R. ranging from 11 to 13. Spark ignition was by two plugs, both rated as relatively cool varieties, namely Autolite B.T.4 and T.T.4. It became of interest, therefore, to carry out experiments with pairs of spark plugs of widely different ratings on a commercial heat scale.

The temperature attained by a spark plug depends on the running conditions of the engine in which it is used. The scale used for the heat rating of spark plugs cannot therefore be one of temperature. It can at best indicate relative temperatures that would be attained by different varieties in similar conditions of use. The spark plugs selected for experiment were:

- 18 mm. Champion R.2.S., rated at bottom of scale,
- 18 mm. Autolite B.T.4, rated at mid position of heat scale,
- 18 mm. " B.T. 10, rated at top of heat scale.

The 18 mm. spark plugs were used in the standard C.F.R. position opposite the bouncing pin which was replaced by a second spark plug of the same heat

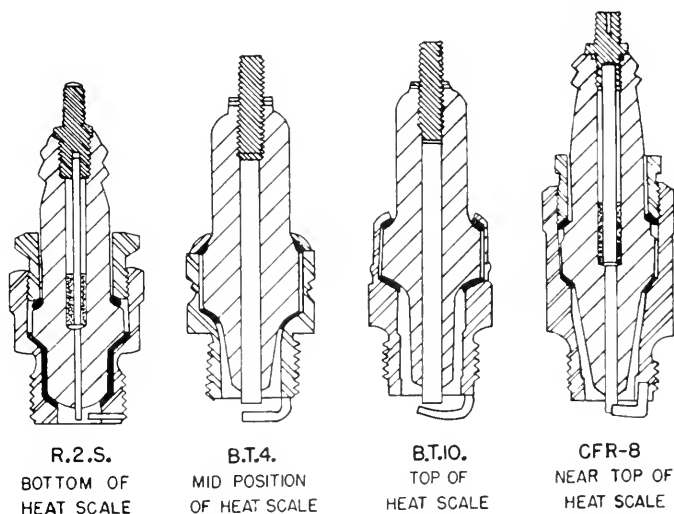


FIG. 13. Diagrams of spark plugs of varying positions on a commercial heat scale, showing the respective areas of exposed core surface.

rating as that of its opposite number, but of the larger size as required for the 7/8 in. bouncing pin hole. The R.2.S. plug was obtainable in the 18 mm. size only and the one used in the bouncing pin hole was fitted with a bushing. The B.T.4 and B.T.10 plugs are obtainable in the 7/8 in. size and are then described as T.T.4 and T.T.10. Thus the experiments were carried out with pairs of low, medium, and high temperature spark plugs. The plugs are illustrated by the diagrams of Fig. 13. It will be seen that the designs are such that the temperatures attained by the ceramic cores are controlled mainly by the areas exposed to flame temperatures. Thus the core of the low temperature plug R.2.S. is copper jacketed leaving the end only exposed to flame. The medium temperature plug has a larger area of core exposed to flame temperature and the high temperature plugs T.T.10 and C.F.R.-8 still larger areas so exposed.

Experimental Results, After-ignition and Preignition

Some degree of after-ignition occurred in the hot engine running conditions of the experiments of Section (2) on raising the C.R. to 13.0. The I.M.E.P. then attained a maximum of 151.0 lb. per sq. in. for a mixture 15% rich. The experiments of this section with pairs of low, medium, and high temperature spark plugs were carried out in similar hot engine conditions but with C.R. raised to the higher value of 14.0. Benzene-air mixtures varying from the

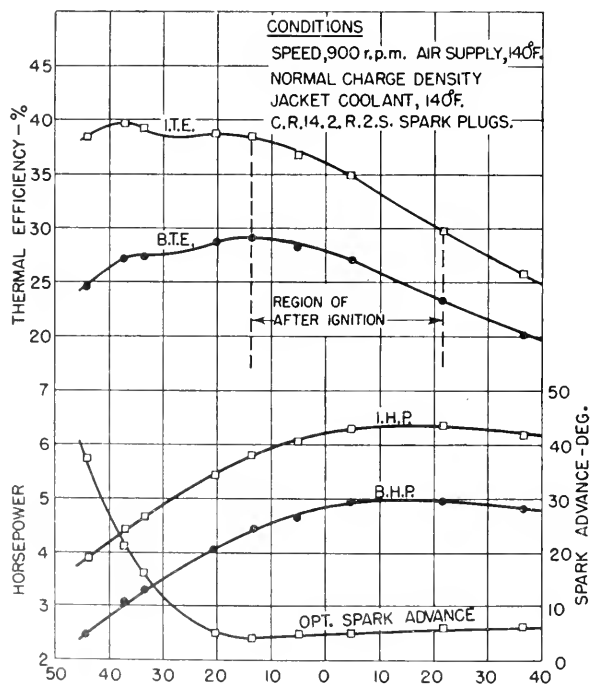


FIG. 14. Hot engine performance in terms of thermal efficiency and power at 14.2:1 C.R. Showing region of after-ignition when using spark plugs at bottom of heat scale.

weakest practicable to 10% rich were used. Spark advance was always adjusted for maximum power output, that is to an optimum value.

Low temperature spark plugs. A pair of R.2.S. spark plugs was used. Spark ignition was required to maintain continuous running over the M.S. range. The values obtained for thermal efficiency and power are given by the graphs of Fig. 14. I.M.E.P. attained a maximum of 149.6 lb. per sq. in. for mixtures 15% rich and I.T.E. was then 33%. The engine ran without spark ignition over a M.S. range of from 11% weak to 22% rich, but with progressively decreasing power until ignition failed after a few seconds. The igniting effect obtained without spark was therefore characteristic of after-ignition.

Medium temperature spark plugs B.T.₄ and T.T.₄. On changing to these higher temperature spark plugs, the engine still required spark ignition for continuous running when using values of mixture strength within the range used for the experiments. Running without spark ignition was however possible with mixtures 26% weak, that is on mixtures leaner than when the low temperature plugs were used. Power decreased progressively, without spark ignition, and, as before, ignition failed after a few seconds; an effect again characteristic of after-ignition. The values obtained for thermal efficiency and power are given by the graphs of Fig. 15. It will be seen that maximum power was obtained when using a mixture 20% rich. The I.M.E.P. was then 153.2 lb. per sq. in. The graphs for thermal efficiency exhibit a double inflection

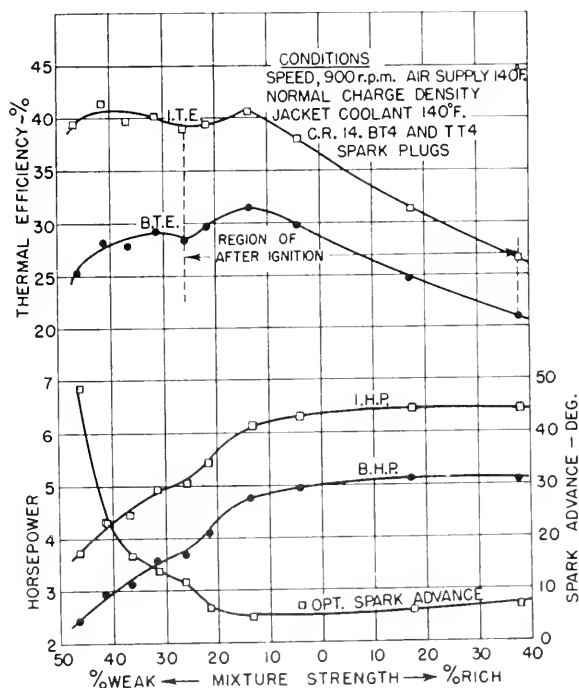


FIG. 15. Hot engine performance in same conditions as used for Fig. 14, but showing increase in region of after-ignition when using spark plugs in mid position on heat scale.

for mixtures ranging from 10 to 47% weak, with a maximum I.T.E. of 41% being obtained for a mixture 14% weak and again for a mixture 40% weak. A similar but less pronounced double inflection was obtained when the cooler spark plugs were used, see Fig. 14.

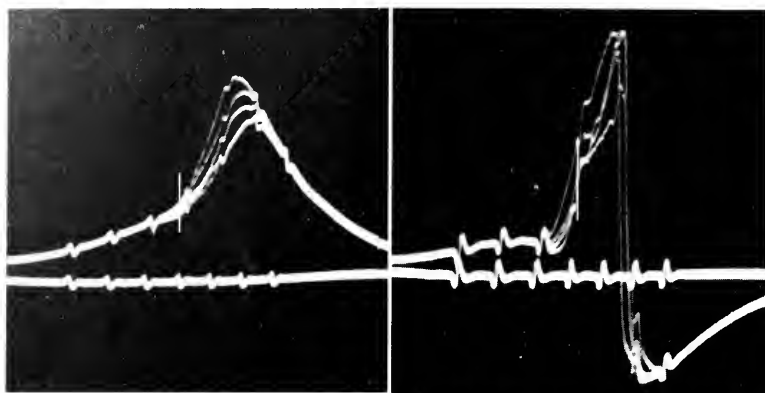


FIG. 16. Pressure-time and rate of change diagrams taken when using spark plugs at top of heat scale and a mixture 16.5% weak in order to show the initiation of preignition on raising C.R. to 10.5, hot engine.

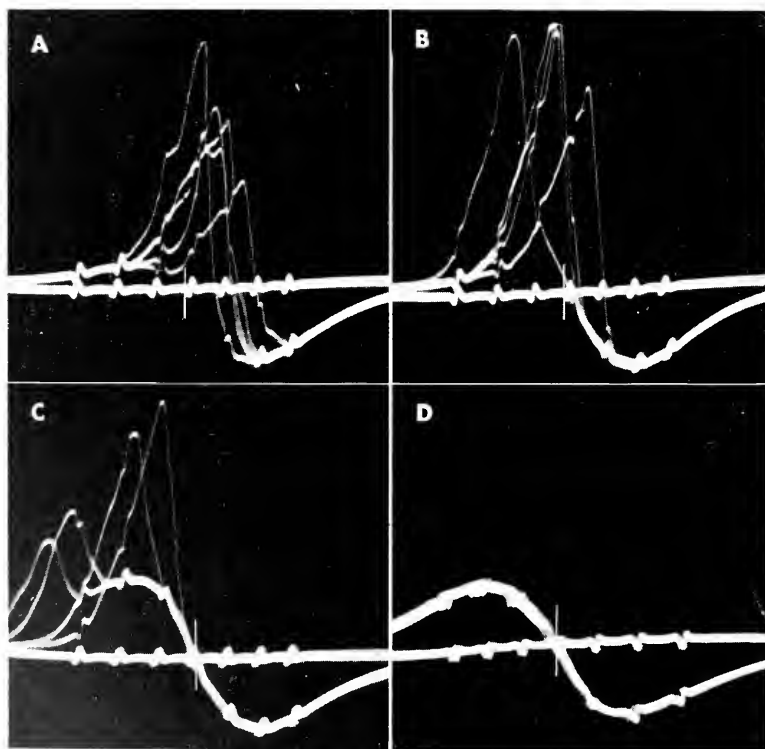


FIG. 17. Rate of change diagrams taken at 10 sec. intervals to show the development of runaway preignition with top of heat scale spark plugs, hot engine, two high temperature spark plugs, C.R. 11:1, mixture 16.5% weak.

High temperature spark plugs, B.T.10 and T.T.10. It was found, on raising the C.R. from a relatively low value, that after-ignition began at a C.R. of 10.5 with a mixture 16.5% weak. The I.M.E.P. was then 125 lb. per sq. in. Time of occurrence in terms of degrees of crank angle before t.d.c. tended to advance with running time as shown by the pressure time and rate of change diagrams of Fig. 16. The C.R. was then raised to 11.0 and runaway preignition occurred. This was accompanied by such heavy pounding that damage to the engine was threatened. It was possible however to take the four rate of change diagrams of Fig. 17, at less than 10 sec. intervals, before preignition occurred so far in advance of t.d.c. that the engine stopped. Referring to the diagrams *a, b, and c* of the figure it will be seen that each includes four combustion cycles. All show the extreme irregularity of the timing of preignition. The maximum advance in timing, diagram (*a*), was 20° before t.d.c. It was 35° before t.d.c. in diagram (*b*) and more than 50° before t.d.c. in diagram (*c*). The time base of this diagram extended over the rounded boundary of the oscilloscope screen and therefore ceased to be linear. Diagram (*d*) was taken when preignition was occurring so far in advance of t.d.c. that the engine was about to stop.

SECTION (4). DISCUSSION

The object of the experiments with benzene was in part to obtain the data given by the graph of Fig. 7, in order that a comparison might be made with similar data obtained for the normal paraffins, heptane, hexane, and pentane, when used in the same conditions of cool engine operation. The values for I.T.E. determined for benzene in these conditions were relatively low as shown by those obtained when the engine was operated in normal temperature and charge density conditions and at 900 r.p.m. Compare Graphs A and B of Fig. 11. The proposed comparison requires some consideration of the factors which govern thermal efficiency and will be given in a subsequent Part in a manner similar to that used in Part XX (2) for fuels containing oxygen in the molecule. In the meantime it is of interest to discuss certain characteristics of the combustion of benzene as developed in the course of the experiments described in Sections (1) to (3).

Comparison of Experimental Results with Those Given in Part XVI

The experimental results of this Part were obtained in engine operating conditions not comparable with those used for the experiments with benzene described in Part XVI (3). In the earlier experiments an endeavor was made to impregnate benzene-air mixtures with finely divided carbon derived from the burning of extremely rich mixtures. The carbon so derived was deposited as soot on surfaces in the combustion chamber. It was expected that dispersion of the soot by initial turbulence would provide a sufficient concentration of carbon nuclei in the end gas to account for the knocking combustion that occurred. The expectation was confirmed by finding that knock intensity observed after a layer of soot had been formed when using overrich mixtures

diminished as the soot was consumed when the engine was run on mixtures containing an excess of oxygen. The experiments of this Part were carried out in conditions which tended to avoid the formation of soot by the burning of the benzene, and ignition was then not obtained otherwise than by a spark or by an overheated surface in the combustion chamber.

Carbon Formation

The expectation that carbon would be formed on the combustion chamber surfaces of the cool engine to a greater extent than on those of the hot engine was not borne out by the results of special experiments. These were made with a C.R. of 8.0 and were begun with a clean engine and with the weakest mixture for which spark ignition was regular. The M.S. was increased by steps to a value 75% rich and the combustion chamber surfaces examined with the aid of an inspection lamp after the engine had run for 30 min. on every M.S. used.

The deposits formed at particular values of M.S. were seen to be similar in both the cool and hot conditions of engine operation. After running on mixtures leaner than correct, the piston crown and other surfaces that could be seen had become coated with a brownish red, rustlike deposit which was little more than a surface color. As M.S. was increased from correct to 50% rich, a very thin layer of hard brownish black carbon formed on the combustion chamber surfaces other than those of the exhaust valve and spark plug core. A layer of soot began to form when M.S. exceeded 50% rich until at 75% rich, all surfaces including those of the exhaust valve and spark plug core were covered by it, and on going to still richer mixtures the engine stopped because of the short-circuiting of the spark plug.

Combustion Knock

When the engine was used in the cool running conditions, Section (1), it will be remembered that optimum values of power and thermal efficiency were obtained when spark timing was fixed at 20° advance and that a considerable pressure rise due to combustion of the fuel occurred before t.d.c. (see indicator diagrams, Figs. 1 and 3). Combustion knock then became audible when M.S. was increased from 38% to 29% weak. Knock intensity increased as mixture strength was further increased and became medium to heavy in the neighborhood of the correct mixture, although C.R. was reduced from 15.0 to 10.0 on increasing M.S. from 39% weak to correct. The increase of knock intensity in the circumstances is attributed to the increase of the combustion pressure that occurred before the piston arrived at t.d.c.

When using the hot engine, with optimum spark advance, increase of pressure due to combustion of the benzene occurred mainly after t.d.c. and combustion was nearly silent even when using correct mixtures. Combustion knock became evident at correct mixtures and values of C.R. higher than 11.0, with the onset of ignition by hot surfaces, and as shown by the experiments of Section (1), developed into the severe type of preignition if high temperature spark plugs were used.

Relative Performance of Engine in Cool and Hot Conditions

The relatively inferior performance of the engine in cool conditions of operation is attributed to the slow burning of the benzene which rendered it impossible to prevent the occurrence of combustion pressure prior to t.d.c. when spark timing was adjusted for maximum power output as explained earlier. The extent of the improvement in performance obtained on changing from cool to hot running conditions is shown for example by comparable experiments made at a C.R. of 8.0 with approximately correct mixtures and spark timing adjusted for maximum power. The experimental results are given by the data of Table V.

TABLE V

ENGINE PERFORMANCE IN COOL AND HOT CONDITIONS, C.R. 8.0, CORRECT MIXTURES

	Spark advance	Maximum combustion press.	B.H.P.	I.H.P.	I.T.E.
Cool engine 400 r.p.m.	11°	12 $\frac{1}{2}$ after t.d.c.	1.30	1.73	29.3%
Hot engine 900 r.p.m.	15°	12 $\frac{1}{2}$ " "	1.39	5.70	32.9%

The data of Table V show that on changing from the cool to the hot conditions an increase of 12 $\frac{1}{4}$ % in I.T.E. was obtained. This increase is attributed to the increase in the inflammability of the benzene-air mixture due to the higher temperature attained at the time of spark ignition. The rate of burning increased accordingly and on adjusting spark timing for maximum power the increase of pressure due to combustion tended to occur after t.d.c. instead of in large part before, as when the engine was run in the cool conditions. Although the increase in I.H.P. from 1.73 to 5.70 shown by the data of Table V may be attributed partly to the increase of inflammability of the benzene-air mixture, it is due mainly to the increase of speed from 400 to 900 r.p.m. and to the increase of charge density.

The rate of burning of the benzene-air mixture in the engine is related to its temperature at the time of spark ignition. The temperatures at the beginning and end of compression have been calculated on the basis of available data and approximate values are tabulated below for correct mixtures used at a C.R. of 8.0.

TABLE VI

ESTIMATED COMPRESSION TEMPERATURES, IN °F.

	Temp. of air supply	Jacket coolant	Compression temperatures	
			Initial	Final
Cool engine, 400 r.p.m.	50	100	100	710
Hot engine, 900 r.p.m.	140	140	200	930

The estimated increase of charge temperatures from 740 to 930°F. due to changing from the cool to the hot running conditions is in accordance with the increase in rate of burning as shown by indicator diagrams. No other data are available for the relation between rate of burning and the temperature of benzene-air mixtures in engine conditions.

Spark Ignition Delay Period

The data of Table V show that the total times in degrees of crank angle taken from the passage of the spark to the attainment of maximum combustion pressure were 23° and 27.5° in the cool and hot running conditions, respectively. If the results of Ricardo's experiments on spark ignition, as quoted by Pye (6, p. 124), be taken to apply to the presently described experiments with benzene, the degrees of crank angle given above as required for the development of maximum combustion pressure should be corrected for the degrees of delay period when there is no appreciable increase of pressure after passage of the spark. According to Ricardo's experiments, the delay period, or "build-up" time, taken in seconds, is independent of engine speed. It was found by him to be represented by 10° of crank angle at 1000 r.p.m. and 20° at 2000 r.p.m. It would on this basis be 9° and 4° respectively at 900 and 400 r.p.m. The corrected times for the development of maximum combustion pressure are therefore 19° and 18.5° of crank angle for the cool and hot running conditions, respectively. The time required for the burning of the benzene to attain maximum combustion pressure was then 0.0029 sec. in the hot and 0.0067 sec. in the cool running conditions.

The ratio of the times is 2.38 and that of the speeds is 2.25. The results appear to confirm approximately the conventional theory as stated by Pye, "that as engine speeds increase so also does the turbulence and the rate of pressure rise, so that the number of degrees of crank angle revolution occupied by the rise remains substantially constant." The sole evidence given in support of the theory is that obtained by Ricardo on increasing the speed of the E.35 engine from 1000 to 2000 r.p.m. while using the M.S. for maximum power and optimum spark advance. The heat load would have been nearly doubled in the circumstances. The consequent increases in charge temperature and the corresponding rate of burning were probably more important than the increase of turbulence in maintaining a constant relation between the rate of pressure rise and the degrees of crank revolution required for the attainment of maximum combustion pressure.

Turbulence created by the mixture passing the inlet valve is probably proportional to engine speed but that existing near the end of compression when the spark passes is what remains after the density of the working fluid has been increased by compression and its viscosity by the rise of temperature due to compression. It cannot, therefore, safely be assumed that turbulence at or near the end of compression increases in direct proportion to engine speed. Directed movement of the working fluid containing small-scale turbulence would be required for the consequent rapid spread of flame. The existence of this type of turbulence is not compatible with the establishment of

the definite flame front which is known to exist between the burned and unburned mixture when combustion chambers are of the nonturbulent type, such as those of the E.35 and C.F.R. engines.

The experiments with benzene indicate that the length of the delay period and the time required thereafter for the attainment of maximum combustion pressure depend on the degree of inflammability of the mixture with air. This factor is related to its temperature as determined by the heat load carried by the engine cylinder.

Heat Load

The term "heat load" as used in earlier text and in this Part is defined as the heat arising from the compression of the fuel-air mixture and the residual gases plus the heat of combustion of the fuel. The heat load increases with engine speed and may therefore be stated in terms of B.t.u. per minute or per cycle. It must be equal in steady running conditions to the rate of heat conduction through the materials of the combustion chamber and the cylinder barrel.

The surfaces of the combustion chamber of an Otto cycle engine are exposed to flame temperatures exceeding 2000°C . during the brief period of addition of the heat of combustion to the working fluid at constant volume. They are then exposed during the expansion stroke to a diminishing charge temperature. However in the running conditions required for maximum power output, the charge temperature at the instant of the opening of the exhaust valve will still be of the order of 800°C . (1408°F .) and will tend to remain at that value during the exhaust stroke. The result will be that on continued running at maximum power output, indirectly cooled materials in the combustion chamber such as those constituting the exhaust valve, the spark plug core, and electrodes will become red hot and the fresh charge may ignite on contact with their surfaces. Ignition may occur during the induction stroke or after the inlet valve closes and the temperature of the charge which includes hot residual gas has been raised by compression. The igniting effect of the exhaust valve or of the spark plug core or of the electrodes is not necessarily dependent on the respective temperatures. The natures and masses of the materials as well as the surface areas must be taken into account. The igniting effect of a particular surface depends also on the nature of the fuel, the mixture strength, and the flow configuration of the combustible mixture in contact with it.

Benzene is not readily decomposed in engine conditions to yield the concentration of nuclei required for autoignition and in consequence the effect of heat load is then in respect of after-ignition, preignition, and rate of burning. Computation of magnitudes of the heat load requires a knowledge of the temperature of the working fluid at the beginning of compression. This temperature can at present be estimated only especially when the fuel enters the cylinder in large part as liquid drops. Estimates of initial and final temperatures of compression are given in Table VI. On the other hand the heat of combustion can be calculated accurately for stoichiometric or

weaker mixtures. The contribution made by the heat of compression is, however, small as compared with that made by the heat of combustion; therefore the total heat load can be determined with a fair degree of accuracy. Estimated heat loads as computed for the C.F.R. engine in significant running conditions used for the experiments described in this Part are tabulated below.

TABLE VII

HOT ENGINE, CALCULATED HEAT LOADS IN B.T.U. PER MIN., BENZENE-AIR MIXTURES, 900 R.P.M., 110 F. JACKET COOLANT, 140°F. AIR SUPPLY, NORMAL CHARGE DENSITY

C.R.	M.S.	Heat of compression, B.t.u./min.	Heat of combustion, B.t.u./min.	Total load, B.t.u./min.	I.T.E., %	Net load, B.t.u./min.
10.0	Correct	120	914	1034	35.3	670
10.0	35% weak	124	494	618	39.0	377

TABLE VIII

COOL ENGINE, CALCULATED HEAT LOADS IN B.T.U. PER MIN., BENZENE-AIR MIXTURES, 400 R.P.M., 100°F. JACKET COOLANT, 50°F. AIR SUPPLY, CHARGE DENSITY 64% OF NORMAL

C.R.	M.S.	Heat of compression, B.t.u./min.	Heat of combustion, B.t.u./min.	Total load, B.t.u./min.	I.T.E., %	Net load, B.t.u./min.
10.0	Correct	34	310	344	29.6	242
13.0	35% weak	45	171	216	34.9	141

It will be seen by reference to the tables that in both cool and hot running conditions, the heat of compression contributed about 10% only to the total heat load when correct mixtures were used but that the contribution was 29% approximately for mixtures 35% weak.

The data of Table VII are comparable in respect of the effect of change of M.S. on heat load. Thus, on increasing M.S. from 35% weak to correct, the heat load increased in the ratio $670/377 = 1.78$. On the other hand it is shown by data given earlier that I.M.E.P. increased in the ratio $144/90.7 = 1.59$. Accordingly, the occurrence of after-ignition and then preignition at values of C.R. higher than 10 as well as the influence of spark plug temperature on these phenomena are attributed to the heat load increasing more rapidly than the I.M.E.P.

The heat load is especially effective in raising the temperature of indirectly cooled surfaces. These, aside from the inlet valve, are the piston crown, the exhaust valve, and the spark plug core. For the hot engine conditions with benzene as the fuel, it is evident from the experiments with preignition, Section (3), that heat load was effective in raising the spark plug core temperature to a level at which the combustible mixture was ignited.

Heat Load and the I.M.E.P. at Which Preignition Occurs

The operating conditions of the C.F.R. hot engine experiments described in this Part were arranged intentionally to be comparable with those used by

Ricardo (7, p. 144) when running the E.35 engine. Ricardo ran his engine at 1500 r.p.m. whereas in the experiments described here, the engine speed was maintained at 900 r.p.m. Two spark plugs were used and the jacket coolant was maintained at the same temperature, namely 146°F. Heat was added to the air supply at the same rate but taking into account the difference in speed, volumetric efficiency, and the volume swept by the piston. The benzene was substantially of the same degree of purity.

Ricardo found that preignition occurred at a C.R. of 6.9. The I.M.E.P. was then 146.5 lb. per sq. in. The variety of the spark plugs is not mentioned in the reference quoted. It is probable that a heat scale was not then available.

When using the C.F.R. engine in as nearly as possible similar thermal conditions but with a C.R. of 14.0, the maximum values of I.M.E.P. were 149.6 lb. per sq. in. with low temperature spark plugs and 153.2 lb. per sq. in. with medium temperature spark plugs. Some degree of after-ignition occurred, but this was not of deleterious effect on power output. When high temperature spark plugs were used, after-ignition was succeeded by violent preignition of the runaway type, as shown by the indicator diagrams of Fig. 17, even when the mixture was 16.5% weak.

An attempt has been made to estimate the heat loads carried by the Ricardo 35 and the C.F.R. engines in terms of B.t.u. per cycle per square inch of combustion chamber surface in similar thermal conditions, allowance being made for the respective ratios of surface area to volume of the combustion chambers. The estimates are tabulated below.

TABLE IX

Engine speed		C.R.	Compression heat, B.t.u./min.	Combustion heat, B.t.u./min.	Total heat load, B.t.u. min.	Net heat load per cycle per sq. in. of surface
E.35	1500 r.p.m.	6.9	600	4615	5215	0.086
C.F.R.	900 r.p.m.	14.0	142	745	887	0.062

NOTE: Values of I.T.E. of 37.2 and 36.6 obtained by experiment for the E.35 and C.F.R. engines respectively were used to obtain net heat loads.

There are no data available at present for the relation between heat load and the temperatures of particular surfaces in the combustion chamber at the time of admission of the fresh charge. Nevertheless, the relative values for net heat load per cycle per square inch of surface, given in Table IX, afford a reasonable explanation for the experimental facts that in the E.35 engine preignition occurred at substantially the same maximum value of I.M.E.P. as in the C.F.R. engine but that a higher value of C.R. was required to obtain the effect in the C.F.R. than in the E.35, assuming that the spark plugs used by Ricardo were not of the highest heat rating.

The combustion characteristics of preignition are illustrated by the indicator diagrams of Fig. 17. They show abnormally rapid pressure changes occurring before t.d.c. and also the rapid advance in the timing of the igniting

effect. There was a consequent increase in the time of exposure of the material of the combustion chamber to flame temperature and radiation. The single cylinder C.F.R. engine stopped before the temperature of indirectly cooled metal parts of the combustion chamber reached the melting points. However on continuing experiments with preigniting fuels other than benzene, the exhaust valve began to burn and its stellite seating loosened. It will be appreciated therefore that if a cylinder in which preignition occurred were one of a supercharged multicylinder engine which continued to run on the other cylinders, burning of the exhaust valve would be extensive and a light metal piston would be liable to melt. This would result in the ignition and explosion, on the opening of the inlet valve, of the compressed mixture in the induction system and the certain wrecking of the engine.

Compression Ignition

Ignition of benzene-air mixtures by the heat of compression did not occur in the course of experiments with the C.F.R. engine described in this Part. An electric spark or a "hot" spark plug was always required. The reason for this, according to the nuclear theory, is that benzene was not decomposed during compression to provide the concentration of combustion nuclei required for an igniting effect, in the conditions of the experiments. On the other hand, explosion (autoignition) of benzene-air mixtures on compression in the M.I.T. single stroke machine is shown by the experiments of Taylor and associates to be preceded by the formation of clouds of combustion nuclei (8, p. 242-247) and it should be possible to obtain a similar igniting effect in an engine in suitable running conditions.

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THE OXIDATION, DECOMPOSITION, IGNITION,
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XXIII. THE EFFECT OF FLOW CONFIGURATION: *n*-PENTANE AND ACETALDEHYDE IN COMBUSTION TUBES OF VARIOUS MATERIALS¹

BY R. O. KING,² S. SANDLER,³ AND R. STROM⁴

ABSTRACT

The experiments presently described are the first of a series intended to elucidate the effect of flow configuration on the velocities of oxidation and decomposition reactions in fuel vapors and gases and on the temperatures of ignition of their mixtures with air. A beginning is made in this Part by describing the effect of flow configuration on the oxidation and ignition of mixtures with air of *n*-pentane and acetaldehyde in a simple form of reactor, namely a combustion tube of large diameter relative to its length. Experiments were made with tubes of materials similar to those in the combustion chambers of engines. The tubes were approximately 1 in. internal diam. and were supported concentrically in a 2 in. diameter vertical furnace with their ends protruding 3 in. from it. There were then steep temperature gradients extending from the midsection of maximum temperature to the relatively cool ends. The combustible gaseous mixture supplied to the lower end of the tube ascended along the wall in a boundary layer approximately 3 to 4 mm. thick and on arriving at the midsection, changed direction, and in large part descended as a central stream which reversed in direction on arriving at the cooler part of the tube adjacent to the lower end of the furnace and then joined the ascending boundary layer. Random turbulence existed between the ascending and descending streams and caused some interchange of gaseous mixture. The convection circulation in the upper part of the tube comprised a descending boundary layer and a central stream ascending to the exit. There was a length of random turbulence between the upper and lower circulations. When the combustion tube was of mild or stainless steel, the velocity of surface oxidation reactions increased as the temperature was raised with the products tending to be carbon dioxide and steam only, and the inflammability of the boundary layer diminished accordingly. Now, because the mixture supplied to the tube goes to the boundary layer its inflammability will increase and its ignition temperature decrease as the rate of mixture supply is increased. Thus when a correct pentane-air mixture was supplied at 100 cc./min. ignition did not occur but on increasing the supply to 200 cc./min. there was explosive ignition at 670° C. Ignition occurred at still lower temperatures on continuing to increase the rate of mixture supply. It occurred at 589° C. when the rate was 475 cc./min. Somewhat higher temperatures were required for ignition in the same circumstances when using a mild steel tube or correct acetaldehyde-air mixtures. When the tube was of carbon or graphite, ignition did not occur even when temperatures were higher than 750° C. and the tubes were being consumed by flameless combustion. The occurrence of ignition in a low-temperature range and again in a high-temperature range is of especial interest in respect of reaction kinetics. The double effect was obtained with either pentane or acetaldehyde in vitreous tubes, but when light metal tubes were used, ignition occurred in the high-temperature range only, with pentane, and in the low-temperature range only, with acetaldehyde. When using a silica tube, ignition of a correct pentane-air mixture occurred in the low-temperature range at 325° C., a temperature at which aldehyde is formed in great profusion by the oxidation of the pentane. When acetaldehyde-air mixtures were used, the preliminary oxidation to aldehyde was not required and ignition in the low-temperature range occurred at 250° C. The respective high-temperature igni-

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tions occurred at 530 and 500° C. Pentane did not oxidize readily to aldehyde in an aluminum tube and ignition occurred in the high-temperature range only, at 646° C., for a correct mixture, but with acetaldehyde, a low-temperature ignition occurred at 364° C. and ignition was not obtained at high temperatures. As a result of these experiments it is concluded that ignition in the high-temperature range, of mixtures with air of either pentane or acetaldehyde, is an effect which depends on the inflammability of the boundary layer and the temperature of the surface over which it is passing. As a further result of the experiments a working hypothesis is advanced for the cause of ignition in the low-temperature range. It is that the reaction leading to ignition is initiated by the peroxides formed after aldehyde has been carried from the boundary layer into the central stream. Whether ignition then obtained was a result of a chain reaction starting from the aldehyde peroxide or a result of nuclei of ignition being formed on the decomposition of the peroxide is an open question. The nuclear theory appears to be the more probable, according to comparable engine experiments.

1. INTRODUCTION

The first experiments on flow configuration, so far as we know, were made by Count Rumford (13), who demonstrated by experiment that the liquid in a vertical glass tube was set in motion as its temperature was raised by heat from an external source, applied *uniformly* over the length of the tube. The motion set up a flow configuration comprising an ascending stream along the wall of the tube and a contraflow along the vertical axis. On the withdrawal of the source of heat the streams reversed in direction as the liquid cooled. Thus was initiated the concept of the transfer of heat by convection; a phenomenon not in agreement with the then-current caloric fluid theory of heat.

The Rumford flow configuration was made visible by the use of a suspension of powdered amber in water, stabilized by the water being brought to the same density as the amber by a suitable addition of caustic soda. The highest temperature of the heat source was that of boiling water and no reaction occurred in the liquid that would liberate or absorb heat. When the temperature of the liquid became equal to that of the uniformly heated wall the previously observed flow configuration disappeared. There would however always be a flow configuration set up by heat convection if the wall temperature were not uniform or if, being uniform, the tube contained a combustible gaseous mixture and heat were liberated by an oxidation reaction occurring on its surface. The tube would then become a reactor such as is commonly used for the study of reaction kinetics by what are described briefly as the "bulb" and "flow" methods.

The bulb method. The combustible mixture is contained in a closed vessel whose surface is heated uniformly as the temperature is raised to initiate reaction. The observed rate of the increase of pressure, due to the reaction, is taken to indicate the rate of the reaction. There will be a flow configuration in the vessel, due to heat convection while the temperature is being raised, and even if the temperature be held constant, the heat liberated by continuing surface oxidation reactions will maintain circulating convection currents. When the experiment is repeated after the vessel has been packed with fragments of its material in order greatly to increase surface area, it is generally found that rate of reaction is reduced, sometimes nearly to zero. It is com-

monly believed that relative values for rates of surface and gas phase reactions can thus be obtained. It is indicated however by experiments described in Part II (5) that reaction in the unpacked vessel occurred in whole or in large part, depending on the nature of the reacting substance, on the heated surface and tended to be inhibited by its own products when the flow configuration was destroyed by packing. The pattern and the magnitude of the flow configuration in a closed reactor would vary with the ratio of surface area to volume, the volume, and geometrical conformation. Reaction rates determined by the closed vessel (bulb) method are known to vary accordingly. Thus the method does not, as is generally supposed, enable a distinction to be made between surface and gas phase reactions.

The flow method. The combustible mixture is supplied continuously to the reactor and the process of raising its temperature by heating the wall of the tube is also continuous. Heat is transferred from the wall to the mixture mainly by circulating convection currents. The corresponding flow configuration becomes stable for any particular temperature level and the corresponding rate of oxidation can be determined by analysis of the exit gases. Experiments with various forms of reactor were described in Part II (5). The flow configuration due to heat convection was varied by changes in the form of the reactor and the ratio of surface area to volume. In some cases it was created in part and in others entirely by passing the reactant through a small orifice into a reactor of relatively small volume, thus forming a flow configuration of the nature of a toroidal vortex. Rates of oxidation observed when using the vortex type of flow configuration were remarkably high and pentane in mixtures with air could be completely oxidized without ignition in a reactor of Jena glass. Further experiments made when using the toroidal vortex type of reactor are described in Part VII (6). The experimental results supported the conclusion that flow configuration is a major factor influencing the velocities of oxidation reactions and corresponding temperatures of ignition.

The Flow Configuration in the Reactors Used for the Experiments of This Part

The experiments were carried out by the flow method and with tubular reactors, described hereafter as combustion tubes. They were always approximately one inch in internal diameter and supported concentrically in a vertical tubular electric furnace of 2 in. internal diameter with their ends protruding about 3 in. The heating coil of the furnace was wound uniformly and was $6\frac{1}{2}$ in. long. The annular space between the furnace wall and the combustion tube was closed at both ends by tightly fitted transite washers. The arrangement ensured steep temperature gradients along the heated tube from the midsection of maximum temperature to the relatively cool ends as shown by the graphs of Fig. 1. It will be noted that the position of maximum wall temperature varies somewhat with the heating current but that it is approximately one inch above the middle section of the length within the furnace.

The gaseous mixture as it passes slowly through the lower part of the tube tends to be heated to the maximum wall temperature and thereafter cooled on passing through the upper part of progressively diminishing temperature

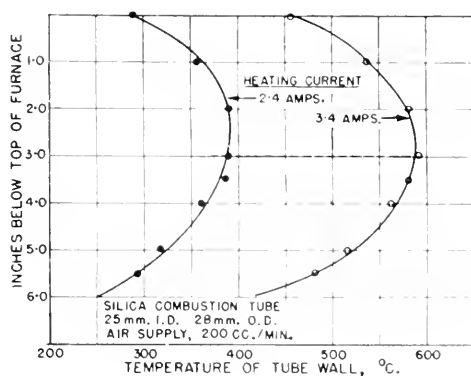


FIG. 1. Temperature gradients along the wall of a silica tube as mounted in the electrically heated furnace.

to the exit. The flow configuration would in general, according to Rumford's experiments, comprise a circulating convection current with a descending central stream in the lower part of the tube and a convection circulation in the opposite direction in the upper part. A more precise knowledge of the flow configuration in the particular combustion tubes used for the experiments was required, especially in respect of the position of the circulations and of the motions which must exist within them.

The pattern of the flow configuration became visible on continuously passing nitrogen containing a small concentration of iron carbonyl through one of the transparent combustion tubes heated electrically by means of an open winding of nichrome strip. The carbonyl decomposed to deposit iron on surfaces at a suitable temperature as would be expected from Callendar's experiments (2). The deposit extended over the entire heated length of the tube at temperatures below 300°C . It is probable that all of the iron in the carbonyl could then have been recovered in the same manner that nickel can be recovered quantitatively from the carbonyl. As the temperature of the midsection of the tube was increased, the tendency of the iron from the carbonyl to deposit thereon diminished. At a maximum tube temperature of 500°C , the deposit remained on the cooler ends only. It could then be seen that the gas in the tube was impregnated with fine particles and tiny flakes of iron, which in spite of their relatively high density were carried by the convection currents to form a pattern of the flow configuration.

The particles in the ascending stream of gas were seen to rise to above the position of maximum tube temperature, then to move toward the longitudinal axis and descend in a well-defined stream to the cooler lower position. The particles did not drop out when the convection current reversed in direction. They either adhered to the surface onto which they were carried or if extremely fine were carried upward by the ascending stream. The thickness of this stream, as estimated by visual observation, appeared to vary from 3 to 4 mm.

A convection circulation was seen to be formed in the upper part of the tube,

near the top of the furnace. This circulation comprised an ascending central stream and a descending stream along the tube wall but was less well defined than that of the reverse circulation below the position of maximum tube temperature.

The experiments indicated that random turbulence prevailed in the spaces between the ascending and descending streams of gas and in the length of tube between the upper and lower convection circulations.

The Combustion Tubes Used as Reactors for the Experiments

The first experiments on flow configuration as described in this part were carried out with combustion tubes of materials similar to those present in the combustion chambers of engines with the object of determining the temperatures at which their surfaces would ignite the fuel-air mixture. The tubes were not obtainable of materials precisely the same as those used in the engine but it was considered that the purpose of the experiments would be served by using generally similar materials, namely, stainless steel (18-8 Cr Ni) to represent exhaust valve material; silica, vycor glass (96% silica), and Pyrex glass to represent the materials of spark plug cores; mild steel, aluminum (97% Al), and magnesium (92% Mg) to represent piston material; carbon and graphite to represent carbonized surfaces. Tubes of the materials mentioned were not obtainable always of the same internal diameter and wall thickness and these dimensions were as given below for the tubes used for the experiments.

Tube material	Internal diameter	Wall thickness	Tube material	Internal diameter	Wall thickness
Stainless steel	28 mm.	1.58 mm.	Aluminum	28 mm.	1.58 mm.
Mild steel	28 mm.	1.58 mm.	Magnesium	28 mm.	1.05 mm.
Silica	25 mm.	1.58 mm.	Graphite	25 mm.	6.4 mm.
Vycor glass	19 mm.	3.2 mm.	Carbon	25 mm.	6.1 mm.
Pyrex	28 mm.	1.58 mm.			

Methods of Measurement and Presentation of Experimental Results

The methods used for the measurement of temperature and the proportion of combustible vapor in the mixtures with air, and for obtaining and analyzing samples of the products of pre-explosion combustion are described in an appendix.

Stoichiometric mixtures are described as "correct" and others as per cent weak or rich according to the percentages by which the combustible vapor is less or more than required for the correct mixture. This mixture contains approximately 2½% by volume of pentane vapor or 8% by volume of acetaldehyde vapor. Rates of supply of mixture to the combustion tube are given in terms of the rates of air supply.

The *n*-pentane was supplied by Phillips Petroleum Co. and the acetaldehyde by the Eastman Kodak Company. Both substances were of Technical grades but were purified by redistillation before use.

The experimental work is described in four sections. Preliminary experiments described in the first were made with combustion tubes of the nine varieties of material in order to determine respective explosive ignition temperatures, denoted hereafter by the abbreviation "E.I.T.". It was disclosed by these

experiments that, excluding the carbon and graphite tubes in which ignition did not occur, the obtaining of significant experimental results required the use of three varieties only of tube material, namely steel, aluminum, and silica. Experiments made accordingly are described in the respective sections III A, B, and C. A discussion of experimental results, given in Section IV, suggests that the reactions which lead to ignition of paraffin hydrocarbons in the gaseous phase are dependent on the formation of aldehyde peroxides (peracids and diacyl peroxides).

II. PRELIMINARY EXPERIMENTS

The Influence of a Variety of Surfaces on Igniting Temperature

The preliminary experiments were carried out with the object of determining the relative effects of the surfaces of the nine available varieties of combustion tube material on the ignition of correct mixtures with air of pentane and acetaldehyde when supplied at 200 cc. min. This rate was selected because when using the steel combustion tubes and lower rates of mixture supply, surface oxidation of the pentane or the acetaldehyde to final products was nearly completed without the occurrence of ignition. It was not possible, for example, to ignite correct mixtures in these tubes when rate of mixture supply was as low as 100 cc. min.

The surface temperatures required for explosive ignition of correct mixtures in the conditions of the experiments are given in Table I. Ignition is described

TABLE I
TEMPERATURES OF EXPLOSIVE IGNITION OF CORRECT MIXTURES WITH
AIR OF PENTANE OR ACETALDEHYDE SUPPLIED AT 200 CC. MIN.

Tube material	Combustible substance	Temperature of explosive ignition
Stainless steel	Pentane	670° C., 1236° F.
	Acetaldehyde	730° C., 1346° F.
Mild steel	Pentane	644° C., 1190° F.
	Acetaldehyde	685° C., 1260° F.
Aluminum	Pentane	646° C., 1195° F.
	Acetaldehyde	364° C., 786° F.
Magnesium	Pentane	615° C., 1139° F.
	Acetaldehyde	349° C., 660° F.
Silica	Pentane	496° C., 926° F.
	Acetaldehyde	237° C., 459° F.
Vycor glass	Pentane	539° C., 1002° F.
	Acetaldehyde	246° C., 475° F.
Pyrex glass	Pentane	493° C., 920° F.
	Acetaldehyde	241° C., 466° F.
Graphite	Pentane Acetaldehyde	Temperatures taken to 750° C. (1382° F.) without explosion
Carbon	Pentane Acetaldehyde	Temperatures taken to 760° C. (1400° F.) without explosion

as explosive when it is accompanied by a flame with rapid burning of the combustible mixture to final products. The nonexplosive type leads merely to partial burning even of correct mixtures and is generally accompanied by "cold" flames. The effect is indicated by pressure oscillations in the mixture flow system, not by a single sharp rise.

Comments on Data of Table I

Stainless and mild steel tubes.—The temperatures of explosive ignition recorded in Table I are higher for the acetaldehyde-air mixtures than for the pentane-air mixtures by margins of 60° C. and 41° C. in the stainless and mild steel tubes respectively. This, in view of recorded igniting temperatures, was an unexpected result. The temperature at which explosive ignition occurs in steel tubes varies with the surface state; a factor depending on the time of use at particular temperatures and the concentration of oxygen in the reacting mixture.

Aluminum and magnesium tubes.—The thermal conductivity of either of the light metals is several times greater than that of steel. It was consequently necessary to fit small water-cooled metal coils to the ends of the combustion tubes protruding from the furnace in order to obtain temperature gradients over the length within the furnace comparable with those along the steel and vitreous tubes. Explosive ignition of the pentane-air mixture occurred at approximately the same temperature as in the mild steel tube, but the acetaldehyde-air mixture exploded in the aluminum tube at temperatures approximately 200° C. lower than in the mild steel tube. The explosion temperatures of 646° C. and 615° C. for the pentane-air mixture are little lower than the respective melting points of the pure metals, 660° C. for aluminum and 651° C. for magnesium. The magnesium tube itself ignited and burned on an occasion when the heating current was not switched off immediately after observing an ignition temperature of 615° C. for a pentane-air mixture.

Vitreous tubes.—The pentane-air mixture ignited and exploded at a temperature of 496, 539, and 490° C. in the silica, vycor, and pyrex tubes respectively. There were, however, slight pressure oscillations accompanied by some luminescence in the temperature range 280 to 320° C., that is, ignition in this lower temperature range was not explosive in the conditions of the experiments. The acetaldehyde-air mixture ignited and exploded at temperatures of 237, 246, and 241° C. in the silica, vycor, and pyrex tubes respectively. An explosive ignition temperature of 240° C. can be taken as an average value. It will be shown later that ignition was nonexplosive for mixtures weaker than correct and that there is another and higher range of temperature over which ignition is explosive for mixtures varying from weak to rich.

Graphite and carbon tubes.—Combustion of the tube material, as indicated by the formation of carbon dioxide in appreciable quantity when air only was passed through the tubes, began at 600° C. and 400° C. for the graphite and carbon tubes respectively. Neither the pentane nor the acetaldehyde mixtures with air ignited when passed through the tubes at the temperatures mentioned. An attempt was made to obtain ignition by raising the temperatures of the graphite and carbon tubes to 750 and 760° C. respectively but was not success-

ful although the tubes were red hot and burning by flameless combustion. The failure is reminiscent of Davy's finding, as quoted by Jost (1, p. 25), that "firedamp (methane) cannot be ignited by flameless burning charcoal". Further experiments with these combustion tubes will be described in a subsequent Part.

Combustion Tube Materials for Further Experiments

The experimental results given in Table I show that similar igniting effects were obtained with silica, vycor, or pyrex tubes, with aluminum or magnesium tubes, and with two varieties of steel tubes. It was considered therefore that the significance of further experiments would not be impaired if combustion tubes of only three varieties of material were used. The varieties selected accordingly were silica, aluminum, and steel.

III. EXPERIMENTS ON THE OXIDATION AND IGNITION OF ACETALDEHYDE AND PENTANE AS AFFECTED BY RATE OF MIXTURE SUPPLY AND MIXTURE STRENGTH

A. SILICA COMBUSTION TUBE EXPERIMENTS

Marcel Prettre (10, 11, 12) was the first to demonstrate by experiment that ignition of mixtures with air of acetaldehyde or of pentane and higher normal paraffins could occur in two temperature stages. It is indicated accordingly that the average values of 237 to 246° C. given in Table I for the explosion of correct mixtures with air of acetaldehyde in vitreous combustion tubes are for first-stage low-temperature ignitions and that relatively high values of 493 to 539° C. given for the explosive ignition of correct pentane-air mixtures are for second stage ignitions.

Prettre used horizontal reaction vessels 120 to 150 mm. long and 60 mm. diam., maintained at a uniform temperature by being placed in mid-position in a long electric furnace. The reacting mixture entered and left the vessel through long capillaries. Thus his experimental method was radically different, especially in respect of the factor of flow configuration, from the combustion tube method used for the experiments described in this Part. It was therefore of interest in respect of reaction kinetics to find out whether ignition would occur in two temperature stages for oxidation reactions in combustion tubes arranged as for the experiments described in Section II.

The silica combustion tube used for experiments with acetaldehyde was 25.0 mm. in internal diameter and had been used for the preliminary experiments of Section II. The tube used for the experiments with pentane was 26.0 mm. in diameter and was new. Air was always supplied at 200 cc. min. and mixture strength was varied by suitable additions of vaporized acetaldehyde or pentane.

Ignition Experiments with Acetaldehyde

First Stage Ignition

Explosive ignition of a correct acetaldehyde-air mixture occurred at 260° C. That is at 23° C. higher than given earlier, Table I. The difference is not significant and must be disregarded because surface action changes in an

unpredictable manner with time of use and other factors and temperatures of ignition vary accordingly. Little change of E.I.T. occurred as mixture strength was increased to 40% rich. Ignition was nonexplosive for mixtures weaker than correct as indicated by the broken line of graph A, Fig. 2, and was not obtainable with mixtures leaner than 50% weak. Oxidation was always accompanied by luminosity before and after ignition in the low-temperature range.

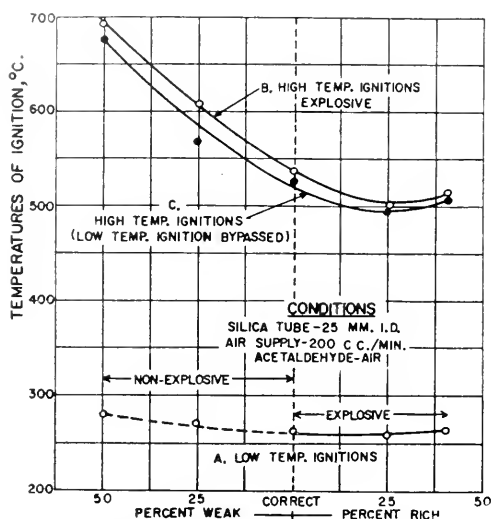


FIG. 2. Ignition characteristics of acetaldehyde-air mixtures in a silica combustion tube.

Second Stage Ignition

The mixtures with air remained luminous as temperature was raised after the occurrence of a first stage ignition. The accompanying slight pressure oscillations disappeared at temperatures approximately 100° C. lower than that of the second stage ignition of a correct mixture. Second stage ignition was always explosive and without premonitory pressure oscillations. The observed values of E.I.T. are given by graph B of Fig. 2. The large variation of E.I.T. with change of mixture strength for mixtures weaker than correct will be noted. Thus E.I.T. was 700° C. for a mixture 50% weak and 540° C. for the correct mixture.

The method of experiment was such that high-temperature ignition might be attributed to the reduction of the inflammability of the mixture due to dilution with combustion products of the previous low-temperature ignition, although temperature was raised slowly after a first stage ignition in the expectation that products of combustion would be cleared from the tube before the occurrence of a high-temperature ignition. It appeared, nevertheless, that confirmatory experiments should be made. The temperature of the tube was therefore raised slowly to 400° C. while air only was passed through it. Acetaldehyde was then supplied at the rate required for a correct mixture and

no explosion occurred until the temperature was increased further to 530°C . High-temperature explosions were obtained in the same manner for mixture strengths of the range of the experiments. The experimental results are exhibited by graph C of Fig. 2. It will be noted that explosive ignition temperatures obtained by the different experimental procedures are in close agreement.

Ignition Experiments with Pentane

First Stage Ignition

The effect was obtained for mixture strengths ranging from 25% weak to 100% rich. It occurred after a period of slowly rising temperature during which faint luminescence could be seen, and was indicated by a single small but distinct pressure "blip", accompanied by the passage of a "cool" flame through the mixture. The nonexplosive first stage ignition temperatures thus determined are given by the broken line graph A of Fig. 3. The temperature of the effect was 325°C . for 25% weak and correct mixtures. It diminished by 15°C . only over the mixture range 25% weak to 100% rich.

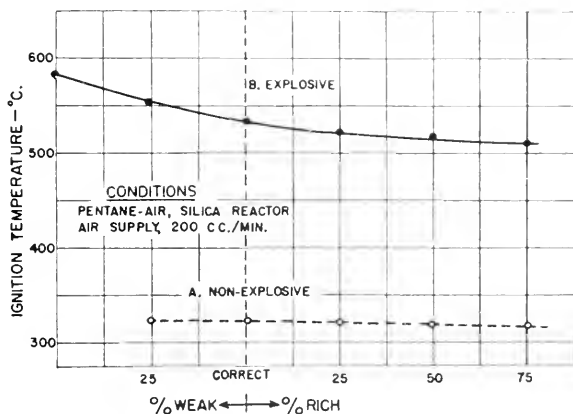


FIG. 3. Ignition characteristics of pentane-air mixtures in a silica combustion tube.

When the tube temperature was raised, luminescence and passages of cool flames continued but with decreasing intensities. The cool flames moved slowly and were not accompanied by pressure oscillations sharp enough to be indicated by the manometer. It was therefore not possible to determine the range of temperature of the first stage of ignition at any particular mixture strength.

Second Stage Ignition

Ignition was explosive over the range of mixture strength used for the experiments, namely 50% weak to 100% rich. Values of E.I.T. are given by graph B, Fig. 3. The E.I.T. for a correct mixture was 535°C . The value observed earlier, Table I, when a different silica tube was used, was 496°C . The experimental results, graph B of the figure, show that E.I.T. increased by 50°C . on the weak side of correct mixture and decreased by 25°C . on increasing mixture strength from correct to 100% rich.

Temperatures of the First and Second Stage Ignition as Affected by Mixture Strength

The graphs of Figs. 2 and 3 show that the temperature of either explosive or nonexplosive first stage ignition of mixtures with air of acetaldehyde or pentane in silica tubes is nearly independent of mixture strength. On the other hand, the temperature of the always explosive second stage ignition of the acetaldehyde increased from $510^{\circ}\text{C}.$ to $700^{\circ}\text{C}.$ as mixture strength was reduced from correct to 50% weak. The temperature of the second stage ignition of pentane increased from $520^{\circ}\text{C}.$ to $585^{\circ}\text{C}.$ in the same circumstances.

Comparison of Second Stage Ignition Temperatures as Given by Figs. 2 and 3 with Those Given by Prettre

It is somewhat remarkable that the graphs of Fig. 2, for the temperatures of the two stage ignition of acetaldehyde, are similar to those given by Prettre (11) for the two stage ignition of pentane. Thus Prettre found that the first and second stage ignitions of a correct pentane air mixture occurred at $260^{\circ}\text{C}.$ and $525^{\circ}\text{C}.$ respectively. The corresponding temperatures determined by the tube method for a correct acetaldehyde-air mixture were $260^{\circ}\text{C}.$ and 530 to $540^{\circ}\text{C}.$, Fig. 2.

The Relation between Wall Temperature and Rate of Oxygen Reacted, Acetaldehyde and Pentane Mixtures with Air

Rates of oxygen reacted as a silica tube was heated to the temperature required for the second stage of ignition of acetaldehyde in three concentrations in mixtures with air are given by the graphs of Fig. 4, and by those of Fig. 5 for four concentrations of pentane in mixtures with air.

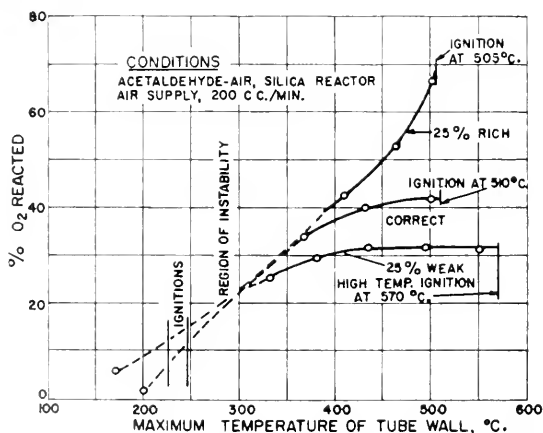


FIG. 4. Percentages of oxygen reacted prior to first and second temperature stages of ignition of acetaldehyde-air mixtures in a silica combustion tube.

Acetaldehyde, Fig. 4

Graphs are given for mixtures 25% weak, correct, and 25% rich. Pressure oscillations of a magnitude to vitiate accurate measurement of rates of acetalde-

hyde supply by the method used began almost immediately after the beginning of the oxidation reaction. The temperature ranges over which accurate measurements could not be made are shown by the breaks in the graphs.

Considering the higher temperature range over which pressure oscillations did not occur and taking r = rate of oxygen reacted, then $dr/dt = 0$ over a temperature range of 130°C . preceding the explosive ignition of the 25% weak mixture at 570°C . When the mixture was correct, $dr/dt = 0$ over the temperature range of approximately 30°C . only, preceding second stage ignition at 520°C . When the mixture was 25% rich, a zero value for dr/dt was never obtained; on the contrary the ratio increased rapidly with increase of temperature and attained the high value of 0.37% of oxygen reacted per $^{\circ}\text{C}$. prior to second stage ignition at 505°C .

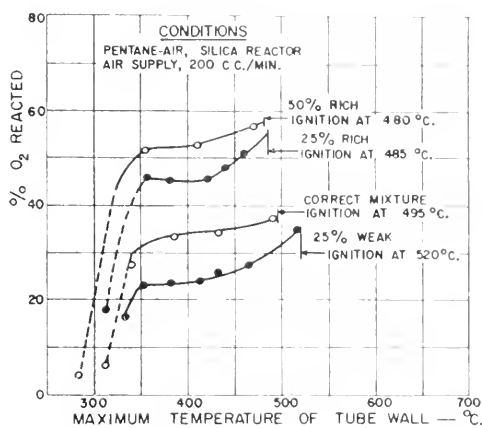


FIG. 5. Percentages of oxygen reacted prior to the second stage ignition of pentane-air mixtures in a silica tube.

Pentane, Fig. 5

The graphs of the figure differ from those of Fig. 4 for acetaldehyde, in that the initial rate of oxidation increases with great rapidity over the temperature range extending to approximately 350°C . Experimental points within this range were not obtained because of the difficulty of accurate observation due to pressure oscillations.

The rapid increase in rate of oxidation below 350°C . is commonly attributed to a correspondingly rapid increase in the rate of formation of aldehydes, water, and organic acids, which reaches a maximum at temperatures in the range 350 to 400°C . In other conditions, such as described in Part II (5), rate of oxidation diminished as temperature was further increased; the temperature coefficient of reaction then became negative.

The second stage ignition temperature given by the graph of Fig. 5 for a correct mixture is 495°C . The ignition temperature for a similar mixture given in Table I is 496°C . The second stage ignition temperatures of Fig. 5 are

however not in close agreement with those given by the graph of Fig. 3. These were however obtained when using a new silica tube of an internal diameter of 26.0 mm.

The Effect of Rate of Supply of Correct Mixtures on First and Second Stage Ignition Temperatures

Correct mixtures with air of acetaldehyde and pentane were used for experiments made at four rates of mixture supply, which as before are stated in terms of rate of air supply. The experimental results are tabulated below. These results were obtained with the new 26 mm. diameter silica tube.

The data of Table II show that in the conditions of the experiments, the temperatures of the first stage ignition of correct mixtures with air of either acetaldehyde or pentane were not affected by increasing the rate of correct

TABLE II
THE EFFECT OF RATE OF MIXTURE SUPPLY ON IGNITION TEMPERATURES

	Rate of supply, cc./min., of correct mixtures and ignition temp., ° C.			
	100 cc.	200 cc.	300 cc.	475 cc.
First stage, acetaldehyde	260	262	268	285
Second stage, acetaldehyde	679	558	542	538
First stage, pentane	321	318	318	322
Second stage, pentane	574	532	532	528

mixture supply from 100 to 475 cc. min. and thereby obtaining a corresponding decrease in time of exposure. The small recorded differences of ignition temperature are within the accuracy of experiment.

The data for the temperatures of the second stage of ignition show on the contrary a considerable decrease of ignition temperature for an increase in rate of correct mixture supply of from 100 to 200 cc. min. The decreases were 121° C. and 42° C. for the acetaldehyde and pentane mixtures respectively. A further increase of rate of supply to 475 cc. min. was of small effect on ignition temperatures.

B. ALUMINUM TUBE EXPERIMENTS

The temperatures of explosive ignition given in Table I are for correct mixtures supplied to an aluminum combustion tube at 200 cc. min. The mixture of pentane with air exploded at 646° C. There was no evidence of a relatively low temperature first stage ignition of the pentane-air mixture. On the other hand, the acetaldehyde-air mixture exploded at the relatively low temperature of 364° C. There was therefore a possibility that a second stage ignition would occur at a considerably higher temperature. An attempt to obtain it was defeated by the melting of the tube.

Effect of Rate of Supply of Correct Mixtures

The values of E.I.T. observed when correct mixtures with air of acetaldehyde and of pentane were supplied to the aluminum tube at 100 to 175 cc. min. are tabulated below.

TABLE III

Rate of mixture supply, cc. min.	E.I.T., °C.	
	Pentane	Acetaldehyde
100	Nil	375
200	616	361
300	629	362
175	620	382

The rate of mixture supply determines the time of exposure of the reacting mixture to the temperature and flow configuration conditions in the combustion tube. It will be noted accordingly that the E.I.T. of the pentane-air mixture decreased as time of exposure decreased in the same manner but to a lesser extent as rate of supply was increased from 100 to 200 cc. min. A further increase in rate of supply to 175 cc. min. and a corresponding decrease in time of exposure led to an increase in E.I.T. of 20° C.

Temperatures of Explosive Ignition as Affected by Mixture Strength

The experimental results given in Table III are for correct mixtures, with rate of mixture supply as a variable factor. Further experiments were made with a particular rate of supply, namely 200 cc. min., and with mixture strength as a variable. The results are given by the graphs of Fig. 6. It will be noted that the E.I.T. for both pentane and acetaldehyde attained a minimum value for mixtures with air approximately 50% rich; the total variation over the mixture strength range 50% weak to 75% rich was 50° C. for pentane, 65° C. for acetaldehyde.

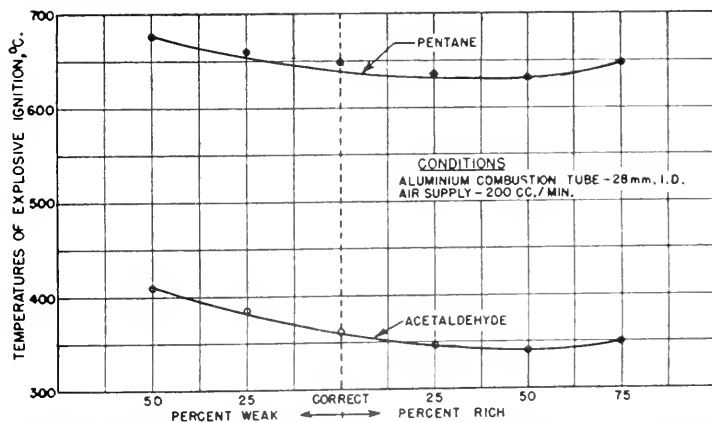


FIG. 6. Explosive ignition temperatures in an aluminum combustion tube as affected by the concentration of acetaldehyde or pentane in mixtures with air.

Ignition of Acetaldehyde in the Aluminum Tube Considered as a First Stage Effect

It was indicated by analyses of samples taken during the experiments made to obtain the data of Table III and of Fig. 6 that the observed ignition temperatures were those of a first stage effect. The temperature of the aluminum tube was therefore raised to 540°C . before a correct acetaldehyde-air mixture was supplied to it at 200 cc. min. Ignition failed to occur although in the earlier experiments, E.I.T. was 476°C . lower at 364°C . The rates of oxygen reacted and of carbon oxides formed when the combustion tube was maintained at 540°C . and rate of correct mixture supply varied from 50 to 200 cc. min. are given by Table IV. Comparable rates are given for correct pentane-air mixtures by Table V.

TABLE IV
CORRECT ACETALDEHYDE-AIR MIXTURES, OXYGEN REACTED
AND CARBON OXIDES FORMED, ALUMINUM COMBUSTION
TUBE AT 540°C . MAX. TEMPERATURE

Flow rate, cc. min.	% O_2 reacted	% O_2 reacted to form CO_2	% O_2 reacted to form CO
50	51.6	20.0	12.2
100	45.0	14.0	11.6
150	44.0	12.3	11.2
200	43.4	11.2	11.0

TABLE V
CORRECT PENTANE-AIR MIXTURES, O_2 REACTED AND CARBON
OXIDES FORMED, ALUMINUM COMBUSTION TUBE AT
 540°C . MAX. TEMPERATURE

Flow rate, cc. min.	% O_2 reacted	% O_2 reacted to form CO_2	% O_2 reacted to form CO
50	44.1	8.7	8.5
100	36.2	7.0	7.4
150	35.6	6.1	6.2
200	33.5	5.5	5.3

It will be seen by comparing the data of Tables IV and V that oxygen was reacted at the greater rate when acetaldehyde-air mixtures were supplied to the tube. The percentage reacted to form carbon oxides was approximately 100% greater than for the pentane-air mixtures. This may be taken to indicate that steam was formed at the greater rate when the acetaldehyde was oxidized.

C. STEEL COMBUSTION TUBE EXPERIMENTS

The temperatures of the explosive ignition of correct mixtures with air of acetaldehyde and pentane supplied to a stainless steel combustion tube at 200 cc. min. were given earlier, Table I, as 730 and 670°C . respectively.

Experiments made with other rates of mixture supply and values of mixture strength are described in this section. In addition to providing interesting data for the relative effects of a steel surface on the oxidation and ignition of acetaldehyde and pentane, the experiments indicate that two stage ignition of both substances might be possible in steel tubes in suitable conditions of flow configuration and temperature.

Effect of Rate of Supply, Correct Mixtures

The values of E.I.T. observed when the mixtures were supplied to a stainless steel tube at 100 to 475 cc. min. are tabulated below.

TABLE VI
EXPLOSIVE IGNITION IN A STAINLESS STEEL TUBE

Rate of mixture supply, cc. min.	E.I.T., °C.	
	Pentane	Acetaldehyde
100	No ignition	No ignition
200	670	730
300	629	696
475	589	662

It will be noted that in the flow configuration conditions of the experiment, the values of E.I.T. for both substances diminished with decreasing time of exposure. Ignition did not occur with the relatively low rate of mixture supply of 100 cc. min. and as the rate was increased from 200 to 475 cc. min. values of E.I.T. diminished by 81 and 68° C. for pentane and acetaldehyde respectively.

Rates of Pre-explosion Oxidation

A series of experiments was carried out at rates of correct mixture supply ranging from 100 to 475 cc. min. Combustion tube temperatures were raised slowly by successive steps until explosion occurred or the limit of temperature measurement was reached. Tube temperature and rate of mixture supply were stabilized at every step while samples of the gases passing out of the tube were taken for analysis. The graphs of Fig. 7 for the relation between percentage of oxygen reacted and maximum tube temperatures with a rate of mixture supply of 200 cc. min. are typical of the series. The rates of oxygen reacted at E.I.T. for the several rates of mixture supply used for the experiments as given by the series of graphs are tabulated below.

The analysis results given in Table VII show that reaction of the oxygen in the mixtures when they were supplied at 100 cc. min. went substantially to completion without the occurrence of ignition. The reaction of the oxygen was little less than complete when the mixtures were supplied at 200 cc. min. and values of E.I.T. of the correct mixtures with air of acetaldehyde and pentane were 730 and 670° C. respectively. However on increasing rates of mixture

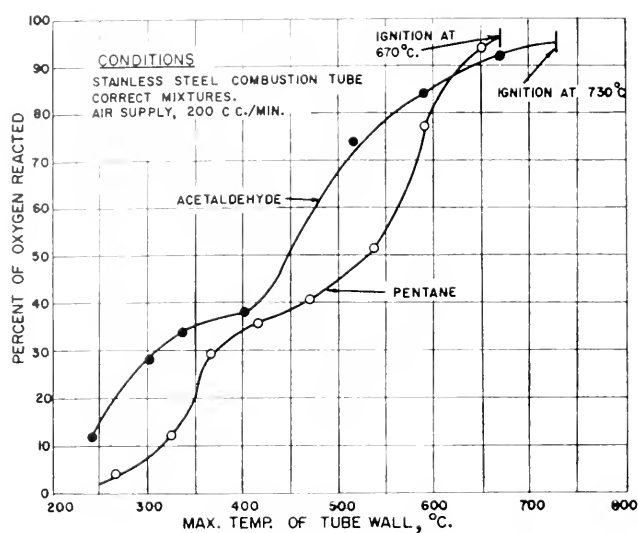


FIG. 7. The relation between percentage of oxygen reacted and the maximum temperature of a stainless steel combustion tube, correct mixtures with air of acetaldehyde and of pentane supplied at 200 cc./min.

TABLE VII
RATES OF OXYGEN REACTED AT TEMPERATURES OF THE EXPLOSIVE
IGNITION OF CORRECT MIXTURES OF ACETALDEHYDE
AND PENTANE WITH AIR

Rate of mixture supply, cc./min.	Acetaldehyde		Pentane	
	E.I.T., °C.	% O ₂ reacted	E.I.T., °C.	% O ₂ reacted
100	None	96	None	99
200	730	95	670	96
300	700	90	629	86
475	662	68	589	62

supply to 300 and 475 cc. min. significant decreases in rates of oxygen reacted, which corresponded with decreases in the temperatures of explosive ignition, were obtained. The experimental results show also that although the aldehyde was oxidized at a higher rate than the pentane, its ignition required a higher tube temperature.

The rates of oxidation, as given in Table VII, were determined from samples of the exit gases. They are therefore not the rates at the midsection of the tube where the temperature was a maximum and ignition occurred. More significant results for the relative rates of oxidation of acetaldehyde and pentane are given by analyses of samples taken at temperatures ranging upwards from those at which reaction occurs at an appreciable rate. Relative rates of reaction at temperatures rising from 250° C., as given by the graphs of Fig. 7, are given

in Table VIII. It is to be remembered in considering the results exhibited by the table that the correct mixtures of acetaldehyde and pentane contained 8.0 and 2.5 moles of oxygen, respectively, to 1 mole of the combustible substances.

TABLE VIII
PERCENTAGES OF AVAILABLE OXYGEN REACHED IN A
STAINLESS STEEL COMBUSTION TUBE, TEMPERATURE
RANGE 250 TO 600° C., CORRECT MIXTURES WITH
AIR OF ACETALDEHYDE AND PENTANE

Max. temp. of tube, °C.	% reacted of available oxygen	
	Acetaldehyde	Pentane
250	15	2
300	28	8
400	38	34
500	68	45
600	86	82

Effect of Mixture Strength on E.I.T.

The results of experiments made when using a mild steel tube, with a particular rate of mixture supply, namely 200 cc. min., and with mixture strength as a variable factor, are given by the graphs of Fig. 8. They show that for mixtures 25% rich, acetaldehyde and pentane possess the same degree of inflammability, values of E.I.T. being then nearly identical at 680° C.; but as mixture strength is reduced, the inflammability of the acetaldehyde diminishes with greater rapidity than that of pentane. Thus for mixtures 25% weak, a tube temperature of 800° C. was required for the ignition of the acetaldehyde and of 640° C. only for the pentane.

Temperatures of nonexplosive ignition, as indicated by pressure oscillations, are shown by the broken lines of the graphs of Fig. 8. Such ignition occurred in pentane-air mixtures leaner than 50% weak and more than 25% rich and in acetaldehyde air mixtures solely for those more than 50% rich. Non-

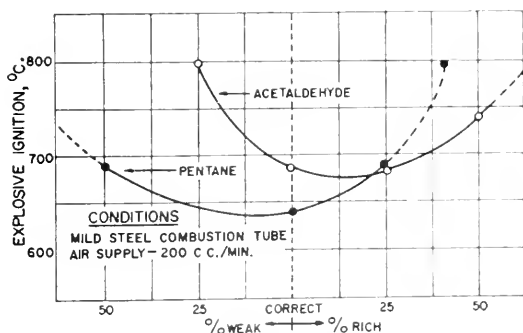


FIG. 8. Temperatures of explosive ignition of mixtures with air of acetaldehyde and of pentane as affected by mixture strength; mild steel tube, mixtures supplied at 200 cc. min.

explosive ignitions are, according to experiments described earlier, indicative of a low-temperature first-stage ignition. A possible explanation of the effect in a steel tube is that when the midsection of the combustion tube is at temperatures of 690°C . and over, as required for explosive ignition, temperature and flow configuration conditions suitable for a first stage ignition may exist in a lower and cooler section of the tube.

IV. DISCUSSION

The gaseous combustible mixture, when ignited in the conditions of the experiments of this Part, was diluted with oxidation products formed during its passage up the combustion tube to the position of maximum temperature. This position varies slightly with furnace temperature but may be described for convenience of reference as the midsection of the length of the tube within the furnace. The midsection temperature required for an igniting effect depends therefore on the degree of inflammability of the mixture at that position. This factor depends in turn on the extent of dilution of the mixture with oxidation products and *their* degree of inflammability.

The oxidation reactions that affect ignition temperature occur therefore below the midsection of the tube. The flow configuration in this length, as determined by experiment, was described in the introductory section. The flow was not unidirectional and laminar with the maximum velocity at the longitudinal axis, as would be expected according to Reynolds Numbers. It formed instead a closed convection circulation with a thin stream ascending along the heated wall and a descending central stream. A state of random turbulence existed between the oppositely moving streams. In these circumstances, the gaseous mixture entering the lower end of the tube necessarily joined the stream ascending along the wall to the position of maximum temperature. This thin stream may be regarded as a boundary layer having temperature gradients both vertically and horizontally. It must therefore be turbulent and as it surrounds the region of random turbulence, there must be a continuous interchange of gas between the oppositely moving streams. The impact of the random turbulence on the boundary layer is considered to be an important factor in respect of reaction velocity. Confirmatory experiments will be described in a subsequent paper.

When a combustion tube is set up concentrically in a vertical tubular furnace and the temperature is uniform at any cross section, the flow configuration in a gaseous mixture passing through it will be determined by the convection currents set up by temperature gradients along the wall and will be symmetrical about the longitudinal axis. The velocities of the convection circulation and the accompanying random turbulence will increase with increase in the temperature gradient. Thus it appeared to be possible, with the rates of mixture supply used for the experiments described in this Part, to heat the gaseous mixture entering the tube at room temperature to that of the midsection, although the heated length of tube below that section and within the furnace was $3\frac{1}{2}$ in. only.

The flow configuration as described would be expected to promote surface oxidation reactions and it is of interest to discuss their influence on the midsection temperature of the tube required for the ignition of a gaseous combustible mixture passing through it. This temperature is necessarily dependent on the degree of inflammability of the mixture in the boundary layer after its passage upward along the tube to the midsection. The reacting substance will then have been oxidized in part to final and partial products, and in similar conditions of flow configuration and rate of supply, the proportion of oxygen reacted and the respective concentrations of the possible oxidation products in the boundary layer will vary with the surface activity of the tube. The consequent phenomena of oxidation and ignition are especially well illustrated by the experiments of this Part with combustion tubes of steel and silica. Flow configuration in these tubes did not differ significantly according to the respective temperature gradients, which tended to become similar as the temperature was raised, and the thermal conductivity of the silica increased while that of the steel decreased.

Ignition in Steel Combustion Tubes

Pentane or acetaldehyde in correct mixtures with air, supplied to either mild or stainless steel tubes at 100 cc. min., was oxidized in the boundary layer so nearly to the final products, steam and carbon dioxide, that ignition was not possible. Ignition of correct mixtures in the stainless steel tube occurred on increasing the rate of mixture supply to 200 cc. min., at midsection temperatures of 670 and 730° C. for the pentane and acetaldehyde mixtures respectively; in the mild steel tube the respective ignition temperatures were lower at 644 and 685° C. respectively, Table I. The respective ignition temperatures in the stainless steel tube, for example, were reduced to 589 and 662° C. on increasing the rate of correct mixture supply to 175 cc. min., Table VI. If ignition had occurred in the gaseous phase as a result of slow combustion therein, the temperature required for the effect would have decreased with an increase in the time of exposure of the combustible mixture to the oxidizing conditions. The occurrence of the opposite effect is attributed to the decrease in the dilution of the boundary layer with final oxidation products and the consequent increase in inflammability as the rate of mixture supply was increased, remembering that the area of active surface remains constant irrespective of the rate of mixture supply. Similarly the acetaldehyde air mixtures required a higher midsection temperature for ignition than the pentane-air mixtures on the steel surface because acetaldehyde was oxidized more rapidly than pentane, see Fig. 7. The experiments indicate that ignition in the steel tubes was an effect depending on the temperature of the midsection of the tube and the inflammability of the mixture in the boundary layer at that position.

Ignition in a Silica Combustion Tube and an Aldehyde Peroxide Hypothesis

Ignition in a silica tube, unlike the effect in steel tubes, occurred in high and low temperature ranges. This phenomenon is attributed fundamentally to

lower activity of the silica surface to oxidize the boundary layer to steam and carbon dioxide than that of the steel surface, and to the increase of the proportion of these final products in the boundary layer with increase of wall temperature. Fluorescence and cool flames were observed in the low-temperature range when mixtures with air of either pentane or acetaldehyde were supplied to the silica tube. A special furnace with a longitudinal slit in the wall was used for the observations. The phenomena have been described by many others and it is generally agreed that they precede ignition in the low-temperature range. In this range ignition in the silica tube appeared by visual observation to occur in the gaseous phase.

There is no general agreement in respect of the mechanism by which an oxidation reaction leads to ignition in the strictly gaseous phase other than that the formation of peroxides of the reacting substance is considered to be essential to a chain reaction mechanism. A comprehensive discussion of the mechanism of ignition in the low-temperature range would require a lengthy review of the work of many others and in any event is best deferred until further experiments on the effect of flow configuration are described. In the meantime a useful purpose will be served by outlining an hypothesis consistent with the results of experiments described in this Part, because it has provided a useful guide for further research. The hypothesis is based on the view that aldehyde peroxides, not alkyl or alkyl hydrogen peroxides as assumed by some (1, 8, 3), are those effective to initiate the reactions leading to ignition in the gaseous phase, and whether the aldehyde peroxides react further by a chain mechanism until ignition occurs as suggested by von Elbe and Lewis (14) or decompose to provide material nuclei of ignition need not be discussed at present.

In applying the hypothesis to the results of the flow configuration experiments of this Part, it may safely be assumed that oxidation started at the source of heat supply, namely the wall of the combustion tube, and that the products were carried from the boundary layer into the central stream by convection currents. The nature of these products is of special significance and has been determined by experiments to be described in a subsequent Part. According to these experiments, the initial products of the surface oxidation of pentane, as found in the boundary layer, tended to be aldehyde and water with traces of acids; there were no peroxides. It must be assumed therefore that peroxides found by analysis of the effluent from the combustion tube are formed by collisions of aldehyde molecules or corresponding acyl radicals carried from the boundary layer into the central stream with oxygen molecules therein.* The consequent oxidation and ignition characteristics of pentane and acetaldehyde, as determined by experiment, will now be discussed.

Pentane Air Mixtures in Silica Tube, Oxidation and Ignition Characteristics

It will be seen by reference to Fig. 5 that reaction began when the maximum

* It should be noted here that generally used methods for the determination of peroxide concentration in combustion products are based on measurements of the active oxygen; thus the nature of the peroxide is not determined.

wall temperature of the tube was approximately 300°C . The reaction was accompanied by the passage of cool flames through the tube and the profuse formation of aldehyde, which is a well-known result of the oxidation of paraffins at relatively low temperatures, and is illustrated by the rapid rate of oxygen reacted in the temperature range 300 to 350°C ., as shown by the graphs of the figure. The aldehyde formed on the surface and present in the boundary layer is, because of the flow configuration, carried into the central stream. The aldehyde peroxides then formed are, according to the hypothesis, responsible for the low-temperature ignition as indicated by the observed pressure waves. These mild and always nonexplosive ignitions were of maximum intensity at a midsection tube temperature of 325°C . for correct pentane-air mixtures supplied at 200 cc./min. , and as shown by graph A of Fig. 3, this value remained nearly constant for mixtures ranging from 25% weak to 75% rich. The fluorescence and the pressure waves tended to die out as the temperature was raised. The concentration of final oxidation products in the boundary layer increased accordingly and pressure waves were not detectible at temperatures higher than 350°C . It will be seen, Fig. 5, that on continuing to raise the temperature, rate of oxygen reacted remained nearly constant until high-temperature ignitions were about to occur. These occurred at temperatures of 505 , 510 , and 570°C . for mixtures 25% rich, correct, and 25% weak, respectively; the temperatures are in fair agreement with those shown by graph B of Fig. 3, for experiments made earlier. The high-temperature ignitions are, as for the steel tube, believed to be a surface effect which depends on the inflammability of the boundary layer at the position of maximum temperature.

The nearly constant rate of oxygen reacted over the temperature range extending from 350°C . to 500°C ., approximately, requires explanation. It is attributed to the negative temperature coefficient of reaction being concealed by surface oxidation reactions occurring over a range of temperature as the boundary layer ascends the temperature gradient of the tube wall. A negative temperature coefficient is usually obtained when the flow method is used and the reactor is uniformly heated as temperature is raised. In these conditions the phenomenon was first observed by Pease (9) and examples of it are exhibited by the graphs of Part II (5).

Acetaldehyde-Air Mixtures in Silica Tube, Oxidation and Ignition Characteristics

The acetaldehyde-air mixtures were supplied to the combustion tube at the rate used for the experiments with pentane, namely 200 cc./min.

The preliminary oxidation required for the formation of aldehyde peroxide from pentane was not required for the experiments with acetaldehyde. Reaction with oxygen started at temperatures approximately 100°C . lower than when pentane was used in similar conditions, compare Figs. 4 and 5. Fluorescence and cold flames appeared immediately, with ignitions occurring in the temperature range 225 to 275°C ., depending on mixture strength, see Figs. 2 and 4. On continuing to raise the temperature, the intensity of the fluorescence diminished as did the magnitude of the pressure oscillations. These effects had disappeared when temperatures attained values of 350°C .

for mixtures 25% weak and 400° C. for mixtures 25% rich. High-temperature ignition of mixtures 25% weak, correct, and 25% rich occurred at 570, 510, and 505° C. respectively.

The results of experiments made to determine definite values for the high and low ignition temperatures for mixtures ranging from 50% weak to nearly 10% rich are shown by the graphs of Fig. 2. The low-temperature ignitions were not explosive for a mixture 50% weak but increased in intensity as mixture strength was increased to become definitely explosive for correct mixtures, and of increasing violence as mixture strength was further increased. This characteristic is due, according to the aldehyde peroxide hypothesis, to the increasing concentration of acetaldehyde in the mixture with air.

The high-temperature ignitions were always explosive. They occurred at temperatures ranging from 500° C. for mixtures 25% rich to 700° C. for those 75% weak. The relation between mixture strength and explosive ignition is similar to that observed for experiments with steel tubes. The experimental results indicate accordingly that high-temperature ignition in the silica tube is as with the steel tube a surface effect occurring at a temperature depending on the inflammability of the boundary layer.

The experiments with acetaldehyde show that ignition in the two temperature ranges does not arise from a common cause, the high-temperature ignition being a surface effect and the low-temperature ignition being an effect in the gaseous phase. They were for this reason obtainable independently as described in earlier text, Section IIIA, and as shown by the graphs of Fig. 2. This characteristic is not apparent when experiments are carried out in closed reactors. The results then obtained appear to show that high-temperature ignition occurs as a consequence of reactions beginning in the low-temperature range.

Ignition in Light Metal Tubes

Similar igniting effects were obtained in aluminum and magnesium tubes. The experimental results given in Section IIIB for aluminum tubes may therefore be regarded as typical. The ignition temperatures for acetaldehyde-air mixtures are little higher than those observed for the ignition of pentane-air mixtures in the low-temperature range, in a silica tube, for correct mixtures; for example, ignition of the acetaldehyde occurred at 350° C., Fig. 6, in the aluminum tube; pentane at 325° C. in the silica tube, Fig. 3. This and the fact that ignition did not occur when acetaldehyde-air mixtures were admitted to the tube after the temperature had been raised to 540° C. indicate that ignition would have been obtained in a higher temperature range if the tube could have been raised to the required degree without melting. The failure to obtain ignition of pentane-air mixtures in a low-temperature range is due, according to the aldehyde peroxide hypothesis, to surface oxidation not providing a sufficient concentration of aldehyde in the boundary layer. This assumption remains to be verified by experiment.

ACKNOWLEDGMENTS

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APPENDIX

Temperature Measurement

A wire ring comprising two chromel alumel junctions in parallel and diametrically opposite was fitted tightly over the combustion tubes at the position of maximum temperature in the annulus between the furnace wall and the outside wall of the combustion tube. Temperatures were measured by using a precision potentiometer to balance the thermoelectric potential against that of a standard cell. Temperatures thus measured were found to be approximately 20° C. higher than those on the inside wall of either a steel or a vitreous tube. The upper limit of temperature measurement was 800° C.

Measurement of Rate of Air Supply

Air used for the experiments was from high-pressure cylinders and was therefore nearly dry. The air from a cylinder discharged through a two stage regulator with an adjustable outlet valve. Fine adjustment of the rate of air flow was attained by using a constant head device consisting of a tee tube having a vertical leg immersed in a water column open to the atmosphere. A nearly constant flow of air at any particular rate was obtained by adjustment of the height of the water column. The air from the constant head device was passed through a drying tower containing "Drierite", and then through a glass capillary tube to the combustion tube. Rates of air flow were determined by measuring the pressure difference across the capillary with a single-leg oil

manometer. Capillaries of required capacities were calibrated by the displacement of water method and by measurement of the rate of travel of a soap film through a calibrated tube.

Measurement of Rate of Liquid Supply

The combustible liquid was supplied by a Rideal microdoser (7). With this apparatus the pressure generated by the gas liberated in an electrolytic cell is transmitted through a liquid seal to a vessel containing the combustible liquid, which is discharged through a capillary into a carburetor where it vaporizes and mixes with the air supply to the combustion tube. Liquid is discharged into the carburetor at a rate governed by the rate of gas liberated in the electrolytic cell and in turn by the electric current passing through it. The liquid seal is in contact with the combustible liquid and should not dissolve it. The seal was of water when pentane was used for the experiments; it was of mercury when acetaldehyde was used.

It has been reported* since the microdoser was described (7) that according to a calibration made by others, the rate of gas liberated in the electrolytic cell does not remain constant for a particular value of the electric current passing through it. The usual method of calibration is to measure the rate at which a thread of mercury is moved through a capillary tube by the gas liberated by a measured current through the cell. The pressures involved are extremely small and on repeating calibrations it was found that results uniformly consistent with Faraday's Law were obtained only when both the mercury and the capillary were chemically clean. Chemical cleanliness is, of course, not of importance when the discharge capillary is filled with liquid which wets the glass. The pressures required to move liquid from the microdoser to the carburetor at small rates of flow, through a short and relatively large diameter capillary, are extremely small. Measurement will therefore not be accurate if pressures in the reactor are fluctuating, as for example when cold flames are passing through the combustible mixture in the reactor. On the other hand, the microdoser provides a useful visual indication of the presence of the cold flames which precede and follow ignition in the low-temperature range as temperature is raised.

Measurement of Rates of Pre-explosion Reactions

The gaseous mixtures issuing from combustion tubes were passed through three condenser traps. The first was cooled in ice-water. The second and third in dry ice-acetone mixtures. Gas samples were taken from the exit of the third trap through a T-tube bypass into an Orsat gas analysis apparatus for measurement of the rates of oxygen reacted and of the formation of carbon oxides. The samples were analyzed immediately after they were taken. At least 30 min. was required for each sample. There was thus sufficient time for the obtaining of steady conditions of temperature and pressure before another sample was taken at a higher temperature. The process of taking and analyzing samples continued until explosion occurred or combustion tube temperature exceeded that measurable by the thermocouples used.

* Private communication.

THE OXIDATION, DECOMPOSITION, IGNITION, AND
DETONATION OF FUEL VAPORS AND GASES

XXIV. THE ADVERSE EFFECT ON THERMAL EFFICIENCY OF THE
ENDOTHERMIC CRACKING REACTION REQUIRED FOR THE
COMPRESSION IGNITION OF PARAFFIN HYDROCARBONS

By R. O. KING AND A. B. ALLAN

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XXIV. THE ADVERSE EFFECT ON THERMAL EFFICIENCY OF THE ENDOTHERMIC CRACKING REACTION REQUIRED FOR THE COMPRESSION IGNITION OF PARAFFIN HYDROCARBONS¹

BY R. O. KING² AND A. B. ALLAN³

ABSTRACT

The adverse effect on thermal efficiency of the decomposition (cracking) reaction required to produce the nuclei which enable a carburetor engine to run with ignition by compression is demonstrated by the experiments described in the text. For this purpose, values of indicated thermal efficiency determined when using normal varieties of pentane, hexane, and heptane with ignition by compression are compared with those determined when using benzene in comparable conditions of mixture strength and compression ratio. In these conditions benzene does not decompose during compression to the extent required to produce nuclei of ignition and mixtures with air require a spark for ignition, unless in contact with a surface at an igniting temperature. Values of indicated thermal efficiency determined when using the paraffins were from 7 to 8% lower than those obtained when using the benzene, mixture strength being 20% weak in both cases. The adverse effect increased with increase of mixture strength. It was approximately 10% for correct mixtures. Furthermore with nuclear ignition the paraffins could be used at weaker mixtures than was possible for benzene with spark ignition. The experiments indicate that the nuclear ignition of paraffin-air mixtures richer than 20% weak is a single stage effect due to carbon derived from cracking of the paraffin. The ignition of leaner mixtures occurs in two stages, the first being initiated by nuclei of a resinous nature. Residues of these nuclei mixed with carbon formed an adherent coating on surfaces not exposed directly to flame such as the lands between piston rings. The rings became firmly stuck in their grooves which had become filled with the residues. The experiments were carried out at diesel engine compression ratios and the results are believed to be of interest in respect of the fundamentals of combustion in that type of engine.

INTRODUCTION

The operation of a C.F.R.-F2 carburetor engine with ignition by compression when normal varieties of heptane, hexane, and pentane were used as fuels was described in Part XXI (4). The compression ratios required for ignition were comparable with those of diesel engines, as would be expected. They varied with mixture strength and the length of the carbon chain of the paraffin molecule. It was always possible to adjust compression ratio for a maximum power output at any particular mixture strength. The experimental results were consistent with the nuclear theory of ignition, as stated in Part IV (3), namely that the finely divided carbon required for the nuclear ignition of the end gas in a spark ignition carburetor engine is provided by the decomposition (cracking) of paraffinic fuel at the high temperatures and pressures attained.

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On the other hand, it was shown by experiments described in Part XXII (5) that a hydrocarbon fuel such as benzene does not decompose at diesel engine compression ratios in a manner to provide nuclei of ignition. Decomposition if it occurred would, in the first stage, yield hydrogen and diphenyl which is a gas at the required temperatures. Thus in the experiments mentioned, a spark was always necessary for controllable ignition, and uncontrolled ignition tending to develop into preignition occurred when a spark plug core attained the requisite high temperature.

The experimental results of Parts XXI and XXII were in accordance with the well-known tendency of normal paraffins to decompose more readily to carbon and other final products than members of the aromatic series, in similar conditions of temperature and pressure. The decomposition reaction is endothermic and if it occurs during compression in an engine, thermal efficiency would be affected adversely by the heat absorbed. Thus it will be shown by the comparison made in this Part that (1) the thermal efficiencies obtained for the paraffins with compression ignition are lower than those obtained for benzene with spark ignition and (2) the paraffins with compression ignition can be used at mixtures leaner than those at which benzene can be ignited by spark ignition and that in these leaner mixtures nuclear ignition occurs in two stages, the first stage appearing to be due to nuclei containing resinous substances.

Arrangement of Text

Subsequent text is in numbered sections for convenience of reference. The normal paraffins are, when convenient, described as detonating fuels. The terms compression ratio, optimum compression ratio, mixture strength, indicated thermal efficiency, and indicated mean effective pressure are, when convenient, abbreviated to C.R., Opt.C.R., M.S., I.T.E., and I.M.E.P. respectively. Chemically correct mixtures of fuel and air are described as "correct" in the text but the abbreviation "C.C.M." is used on graphs. Values of compression ratio are abbreviated to a single number. Opt. C.R. is the value at which power output is a maximum at a particular mixture strength. Compression ignition is, when the context is fitting, described as nuclear ignition. It is to be understood that values for I.M.E.P. given in the text or on graphs are in pounds per square inch and that values given for engine speeds are revolutions per minute.

Heat Load

This term, although not commonly used, has been adopted as a convenient expression for the factors which determine the mean temperatures attained by surfaces in the combustion chamber, see discussion Part XXII (5, pp. 45-48). Primary factors are: the heat arising from compression of the fuel-air mixture and residual gases and the heat content of the entering mixture; plus the heat liberated by combustion of the fuel; minus the proportion converted into work, that absorbed by vaporization of fuel after admission, and that rejected to the exhaust. The heat load, expressed in B.t.u. per min. at parti-

cular values of C.R. and M.S., is then directly proportional to engine speed at constant volumetric efficiency. It will then be equal to the rate of heat conduction through the materials of the combustion chamber when engine temperatures have reached a steady state. The surface temperatures attained by materials in the combustion chamber will then depend on the temperature gradients in them. These in turn will depend on their thermal conductivities, the length and the nature of the heat path to the cooling medium, and its temperature. The surfaces of indirectly cooled parts of the combustion chamber are most liable to attain temperatures that will affect the combustion of the fuel. These are: the valves, the center of the piston crown, the ceramic core of the spark plug, and its electrodes. Any one of these, with an extremely heavy heat load, may attain the temperature required for some degree of flameless combustion of the fuel, but in normally aspirated water cooled engines, the surfaces liable to attain an igniting temperature in respect of the fuel-air charge are those of the exhaust valve, the ceramic core of the spark plug, and in some cases those of its electrodes—the exhaust valve because it is off its cooling seat during the exhaust stroke, the head and the lower part of its stem being then in the path of the exhaust gases, and the ceramic core of the spark plug because of its low thermal conductivity.

I. RATES OF BURNING OF PARAFFIN-AIR MIXTURES WITH NUCLEAR IGNITION AND OF BENZENE-AIR MIXTURES WITH SPARK IGNITION

Paraffin-Air Mixtures

Experiments with the paraffins, described in Part XXI (6), were carried out in engine conditions of a subnormal charge density, an air supply temperature of 50° F., a jacket coolant temperature of 100° F., and an engine speed of 400. That is, the heat load on the engine was relatively low and the corresponding low cycle temperature would be expected to be of favorable effect on indicated thermal efficiency. Ignition was by compression and maximum power output was obtained for values of the C.R. of 8.5, 9.6, and 10.0 for correct mixtures with air of heptane, hexane, and pentane, respectively. The characteristics of combustion are illustrated by the typical pressure-time diagrams of Fig. 1, taken when using heptane as the fuel. Short vertical lines have been added to the diagrams to mark the "blips" fed into the electronic circuit at 10° intervals of crank revolution by a notched timing wheel. The line at top dead center is marked t.d.c. The irregularity of spacing is due mainly to the inertia of rotating parts, including the armature of the direct connected generator, which was such that the speed of rotation of the blip timing wheel attached to the out-board end of the armature shaft was affected by cyclic changes of pressure on the piston. A relatively thick indicator diaphragm was used when taking diagram A, because of the high pressure developed. Therefore the pressure scale differs from that of diagram B. Both diagrams were taken with a "Sunbury" indicator and consequently the pressure scales are non-linear.

It will be seen by reference to the diagrams that nuclear ignition occurred in a single stage for mixtures correct and 20% weak. It occurred in two stages

for mixtures weaker than can be used for benzene with spark ignition. The characteristics of the two-stage effect will not be discussed at present. Diagram A, for a correct heptane-air mixture, shows that compression pressure ceased to rise appreciably at approximately 12° before t.d.c. and remained substan-

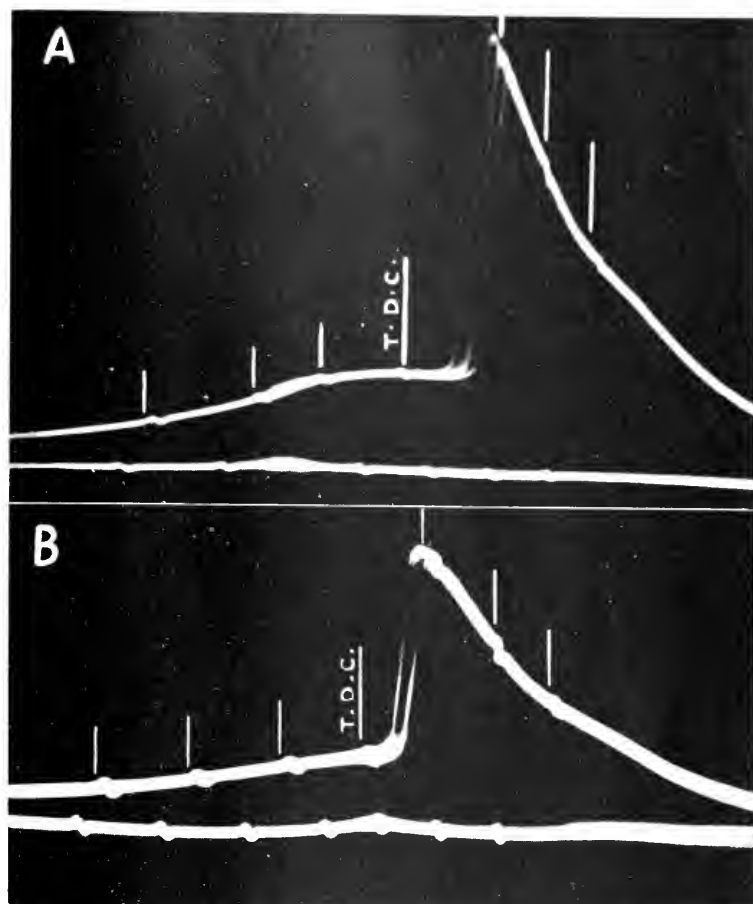


FIG. 1. Typical diagrams for the combustion of paraffins with nuclear ignition.
 A. Correct mixture, C.R. 8.5.
 B. 20% weak mixture, C.R. 9.1.
 Heptane.

tially constant until 7° after. The failure of pressure to rise during 19° of crank revolution is attributed to the absorption of heat by the decomposition reaction required to produce nuclei of ignition. It is the familiar "delay angle" which is a characteristic of the combustion of paraffinic fuels in diesel engines.

The combustion characteristics of the nuclear ignition of the 20% weak heptane-air mixture are shown by diagram B. This diagram, like diagram A, was taken when C.R. was adjusted for maximum power output and it will be

noted that, as for diagram A, this was obtained when combustion pressure attained a maximum value at approximately 10° after t.d.c. The Opt. C.R. was 9.1 and it appears from the compression line of the diagram that decomposition of the heptane at the gas temperatures and pressures attained accordingly began earlier than when the C.R. was lower, at the value of 8.5, as required to obtain maximum power output for a correct mixture, diagram A. A definite value cannot be assigned to the delay angle for the weaker mixture in the absence of a diagram for compression of air only. Both diagrams show that the pressure rise due to combustion started sharply at the end of the delay period, presumably on the attainment of the requisite concentration of nuclei in the part of the combustible mixture at maximum temperature. That would be the part adjacent to the exhaust valve, the spark plug having been replaced by a mild steel blank. The time interval between nuclear ignition and the attainment of maximum combustion pressure was 3° of crank revolution or 0.00125 sec. If the distance of flame travel is taken from the center of the exhaust valve to the farthest point on the combustion chamber wall, the velocity would be 150 ft./sec. In the circumstances and in the cool running conditions, the engine ran on a nearly exact constant volume cycle of relatively low temperature with maximum combustion pressure occurring at the piston position for maximum power output. Indicated thermal efficiency should therefore have approached the ideal value as nearly as possible in practice, *but for the loss during compression and prior to ignition of the heat absorbed by the decomposition reaction required to produce an igniting concentration of nuclei*. This loss would affect compression pressure adversely with the result that the engine would be running on a compression ratio lower than the measured value which is used when calculating thermal efficiency.

Benzene-Air Mixtures

The slow burning characteristic of benzene and its failure to decompose in the end gas of a spark ignition engine to provide the nuclei of ignition required for "detonation" are attributed to the stability of its molecule. A further consequence of slow burning is that in the experiments described in Part XXII (5), benzene was not a good fuel for the C.F.R. engine when operated in conditions of low heat load, in that when an attempt was made, by raising the compression ratio, to obtain maximum thermal efficiency for weak mixtures, the engine tended to run on a constant pressure instead of a constant volume cycle (5, pp. 27-28). An approach to a constant volume cycle was obtained for mixtures in the neighborhood of correct on increasing the heat load by raising the air supply from 50 to 140° F., the jacket coolant from 100 to 140° F., the speed from 400 to 900 r.p.m., and the charge density from 64% of normal to normal. It was estimated that these increases had resulted in raising the initial temperature of compression from 100 to 200° F. and the final temperature from 740 to 930° F. when the C.R. was 8.0 (5, p. 43). The characteristics of combustion obtained accordingly at the C.R. of 8.0 are illustrated by the typical indicator diagrams of Fig. 2. The time of passage of the spark is shown on the diagrams by the small downward blip fed into the electronic circuit. Optimum

spark timing was always used and it will be seen by reference to diagram A, that the spark occurred at 11° before t.d.c. and maximum pressure at 13° after. When a 26% weak mixture was used, diagram B, optimum spark timing was 21° in advance of t.d.c. and maximum combustion pressure occurred at 15° after.

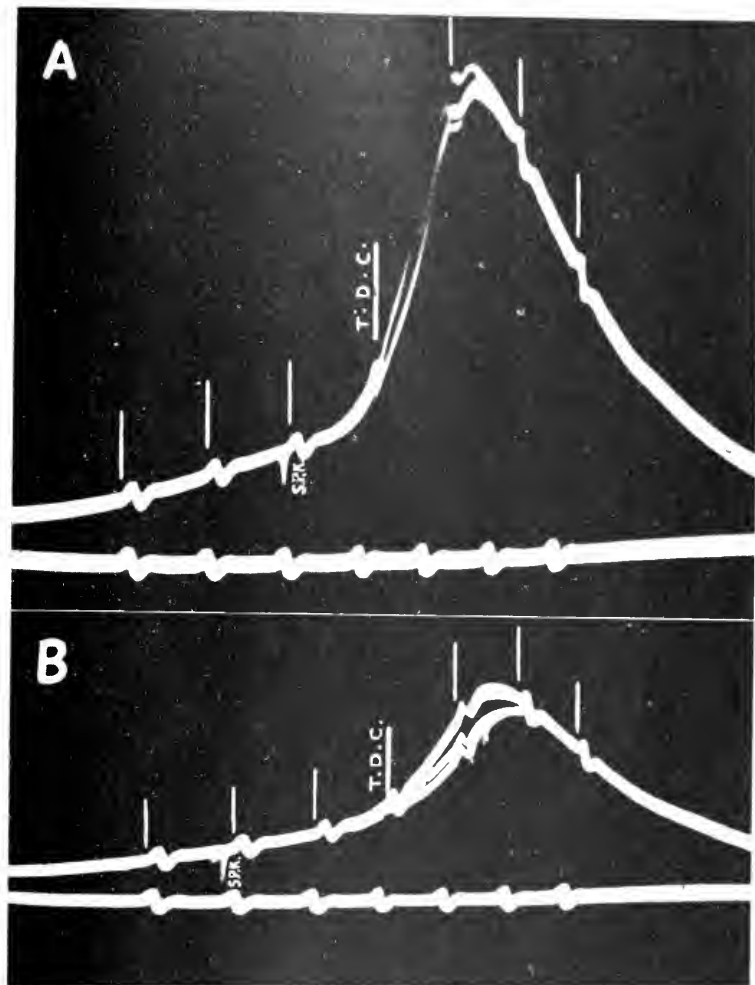


FIG. 2. Typical diagrams for the combustion of benzene with spark ignition.
A. Correct mixture, C.R. 10.
B. 26% weak mixture, C.R. 8.

The long burning time required for the combustion of the benzene-air mixture even after increasing inflammability by raising the temperature of the charge at the time of spark ignition is in sharp contrast with the 3° of crank revolution required for combustion when nuclei of ignition had been provided by the preflame decomposition of a normal paraffin.

II. NUCLEAR IGNITION AND THE RELATION BETWEEN INDICATED THERMAL EFFICIENCY AND COMPRESSION RATIO; PENTANE, HEXANE, AND HEPTANE

It was shown by experiments with the normal paraffins used in engine running conditions in which nuclear replaced spark ignition that the relation between Opt. C.R. and M.S. is represented by a W form of graph instead of the U form obtained when ignition is by spark at relatively low values of C.R., Part XXI (6). The W form of graph shown at A, Fig. 3, is for pentane-air mixtures and is similar in form to those obtained when using hexane and heptane. These will be given later as required. The corresponding relation between I.T.E. and

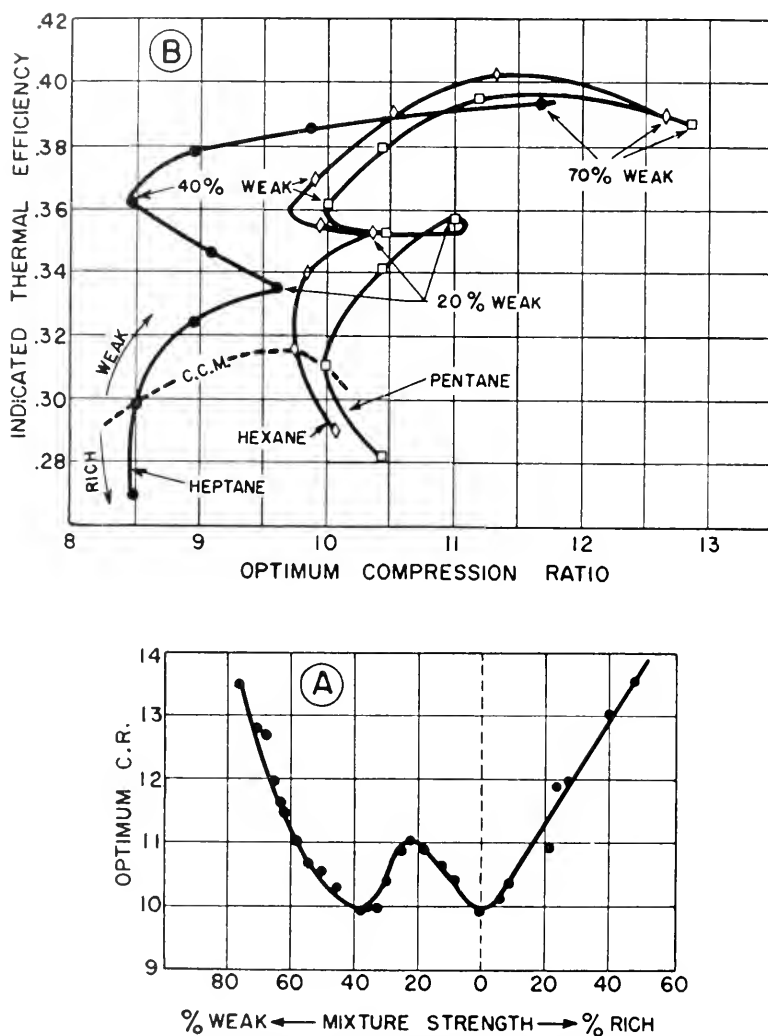


FIG. 3. A. Typical relation between Opt. C.R. and M.S. shown by experiments with pentane. B. Relation between I.T.E. and C.R. with diminishing M.S.; heptane, hexane, and pentane.

C.R. for mixtures with air of pentane, hexane, and heptane ranging from 10% rich to 70% weak, as determined by experiments described in Part XXI, are exhibited by the corresponding graphs, B, Fig. 3. They were not given earlier because comparable results for a non-detonating hydrocarbon with spark ignition were not then available. Experimental points are not shown on the graphs. They have been replaced by points indicating 10% changes of mixture strength. Correct mixtures are indicated by the broken line crossing the graphs.

Indicated thermal efficiency is shown by the graphs to have increased, as would be expected as Opt. C.R. was increased and mixture strength decreased from correct until it became 20% weak. An abrupt reversal of direction of the graphs then occurred and I.T.E. remained nearly constant over the mixture range 20 to 40% weak for both pentane and hexane. It will be noted however by reference to the A graph, that Opt. C.R. ratio diminished over this range of M.S. It appears therefore that the increase in I.T.E. normally due to a decrease of M.S. was just offset by the decrease in I.T.E. due to decrease of Opt. C.R. Nuclear ignition of heptane-air mixtures occurred at considerably lower compression ratios than were required for mixtures with air of pentane or hexane. The adverse effect on I.T.E. of decreasing Opt. C.R. over the mixture range 20 to 40% weak was, as shown by the graph, more than offset by the beneficial effect obtained on decreasing the M.S.

The graphs for I.T.E. show that another abrupt reversal of direction occurred for all three fuels when the mixtures became 40% weak. Then as mixture strength was further decreased and Opt. C.R. increased, I.T.E. increased slowly to a maximum value and then diminished. This characteristic is related to the occurrence of ignition and combustion in two stages, with the first beginning before t.d.c., Part XXI (6, Figs. 3 and 4).

The decomposition of heptane in correct mixtures with air, to provide nuclei of ignition at a C.R. of 8.5 whereas values of C.R. of 9.6 and 10 were required to obtain a similar effect in respect of hexane and pentane respectively affords a rational explanation for the use of heptane to represent zero on the C.F.R.-A.S.T.M. knock rating scale.

III. THERMAL EFFICIENCIES: BENZENE

Indicated Thermal Efficiencies at Values of C.R. from 4 to 13

The values of I.T.E. for benzene-air mixtures varying from 20% rich to the weakest on which the engine would run, and at values of C.R. increasing from 4 to 13, as determined by experiments described in Part XXII (5), are given by the graphs of Fig. 4. The operating conditions were those of the "higher" heat load. There are three features of the experimental results of especial present interest:

(1) The I.T.E. at any particular C.R. increased continuously, although at a decreasing rate as M.S. was reduced, as would be expected, until it had attained a maximum value when it diminished rapidly as misfiring began.

(2) The M.S. for which a maximum value of I.T.E. was obtained diminished with increase of C.R., as shown by the inclined broken line crossing the graphs of the figure. That is, misfiring occurred with progressively weaker mixtures as compression ratio was raised. Thus at a C.R. of 13, smooth running without misfiring continued until the mixture became 35% weak, but at a C.R. of 4, misfiring began with mixtures leaner than 25% weak.

The I.T.E. obtained for a mixture weaker than that required for maximum thermal efficiency is therefore not regarded as a true value.

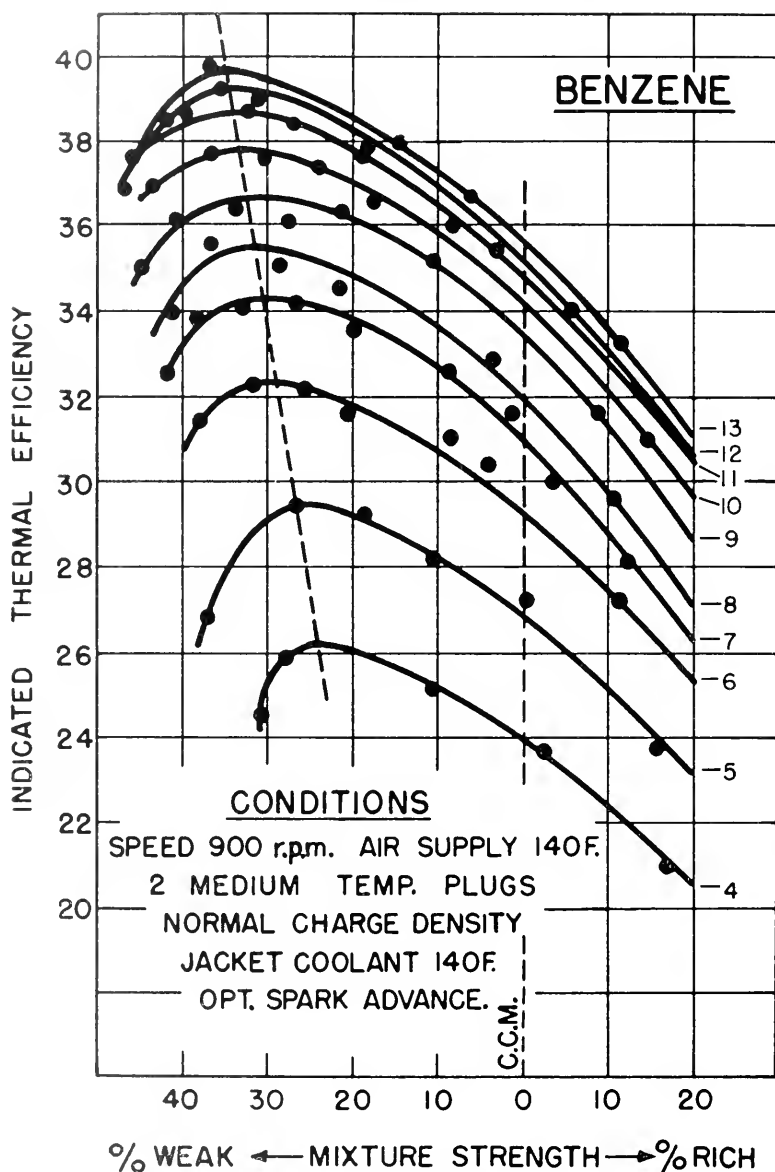


FIG. 4. Relation between I.T.E. and M.S. at values of C.R. of 4 to 13.

Indicated Thermal Efficiency as Affected by Heat Load

It was found as a result of an extensive series of experiments with benzene-air mixtures (5) in the low heat load conditions, that optimum values for I.T.E. over a wide range of M.S. were obtained when spark timing was fixed at 20° in advance of t.d.c. and C.R. always adjusted for maximum power output as M.S. was varied. The relation between Opt. C.R. and M.S. thus obtained is given by graph A of Fig. 5, and the corresponding values of I.T.E. by graph B.

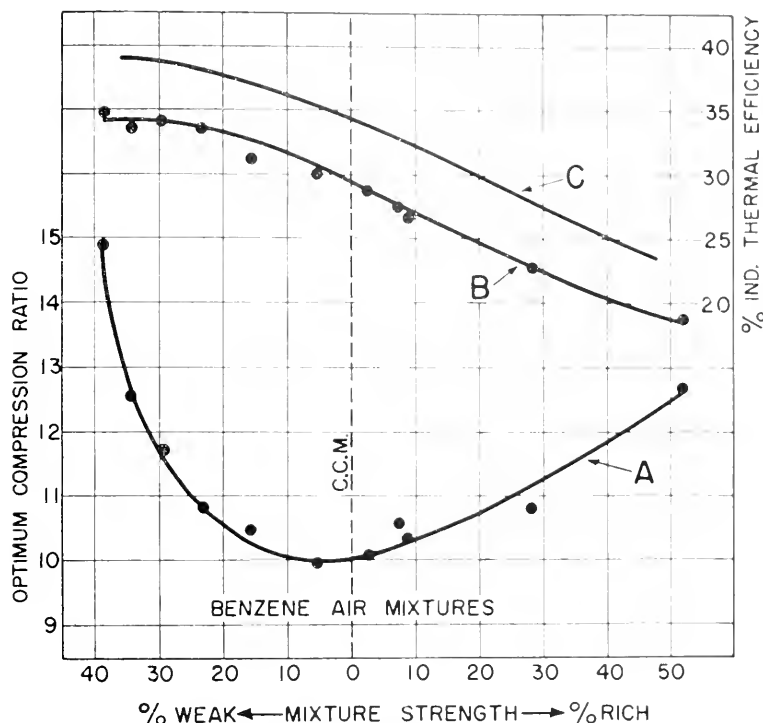


FIG. 5. Heat load, effect on I.T.E.
 C. I.T.E. with high heat load.
 B. I.T.E. with low heat load.
 A. Common base of optimum C.R.

Now by making use of the data given by the graphs of Fig. 4, the I.T.E. values for similar values of M.S. and C.R. as determined in the running conditions of the higher heat load can be obtained. These are given by graph C of the figure and it will be understood that the values of I.T.E. shown by graphs B and C are derived from the common basis of Opt. C.R. and M.S. as represented by graph A. The noteworthy feature of the experimental results is that thermal efficiency increased on increasing the temperature of the cycle. This anomalous result is attributed to the increase in inflammability of the benzene-air mixture due to the increase of heat load and the consequent addition of the heat of combustion of the benzene to the working fluid at more nearly constant volume, this effect being great enough to more than offset the adverse effect of increasing the temperature of the cycle.

Indicated Thermal Efficiencies Compared with Ideal Values

The relation between I.T.E. and C.R. is given by graph A of Fig. 6, for benzene-air mixtures used in conditions of the low heat load and with ignition timing fixed at 20° in advance of t.d.c. A single hot spark plug, C.F.R.-8, was used. There is shown a just measurable increase in I.T.E. for an increase of

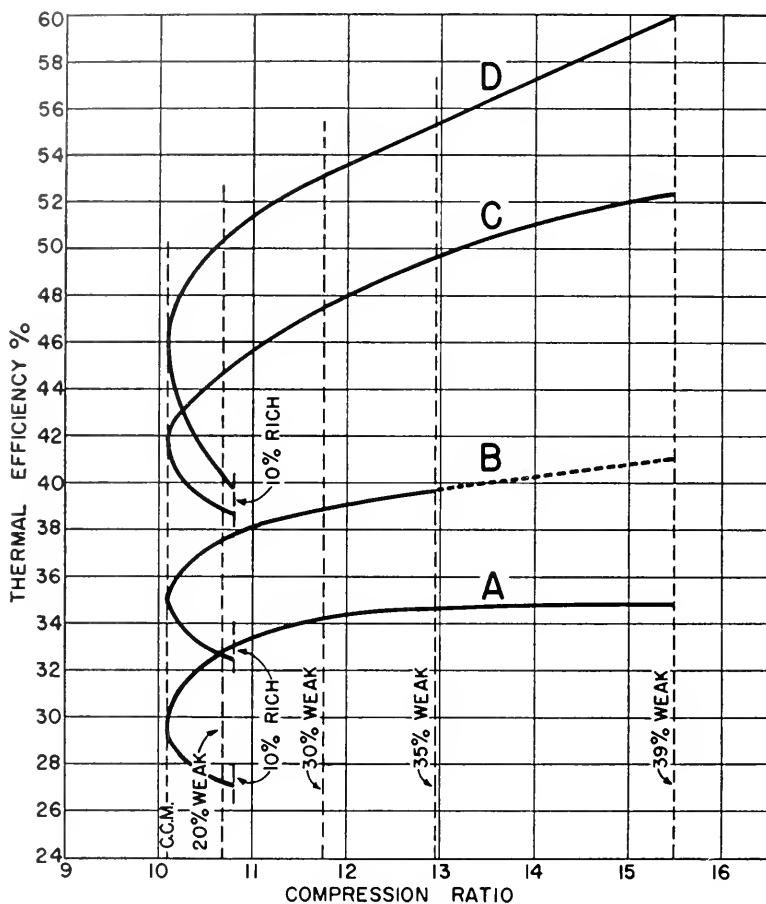


FIG. 6. Observed indicated thermal efficiencies. Benzene-air mixtures compared with calculated ideal values.
 A. Observed, with low heat load.
 B. Observed, with higher heat load.
 C. Ideal, calculated by "Leah" method.
 D. Ideal, calculated by text book method (Pyc).

C.R. from 13 to $15\frac{1}{2}$ and a decrease of M.S. from 35 to 39%. The small increase in I.T.E. in the circumstances is attributed to the slow burning of the benzene. Thus for example, the occurrence of maximum combustion pressure 2 to 3° earlier for a mixture 37.7% weak than for one 23.3% weak, Part XXII (5, p. 29, Table II), is attributed to combustion not having been complete at the

piston position at which it was indicated to have occurred. That is, the cycle was changing from constant volume to constant pressure.

The higher values for I.T.E., graph B, are from the data of Fig. 4 for the results of experiments made in the higher heat load conditions and are for the values of C.R. and M.S. for which graph A was obtained. Although two cooler spark plugs, at mid position on the heat scale, were used, the engine would run on weak mixtures for a short period without spark, graph B, Fig. 6. This igniting effect requires further investigation in view of the possibility that the benzene began to decompose to yield diphenyl and hydrogen at the gas temperatures attained at values of the C.R. higher than 13.

Graph C of the figure is for ideal values of thermal efficiency for benzene-air mixtures calculated by the method devised by Leah (7), and modified to allow for engine speed, cylinder dimension, and particular values of the initial temperature of compression. It is assumed however, as in theoretical calculations by others, that the heat of combustion of the benzene is added to the working fluid at constant volume.

Graph D is for ideal values of thermal efficiency as calculated by Pye (10, p. 181) with the use of the most reliable values for specific heats and dissociation available at the time. No allowance was included for engine speed and dimensions. The initial temperature of compression was taken as 212° F. and the calculations were based on a constant volume cycle.

The graphs of Fig. 6 illustrate the increasing rate of departure of real from ideal values of thermal efficiency, with decreasing concentration of benzene in mixtures with air and the consequential decreasing rate of burning of the benzene-air mixture. They show that deductions, based on the assumption that graphs for the variation of ideal and real values of thermal efficiency with compression ratio lie parallel though separated, as made by Pye (10, pp. 181-183) for example, and others, are not justified.

IV. NUCLEAR IGNITION AND THE ADVERSE EFFECT ON THERMAL EFFICIENCY

The adverse effect is exhibited by the graphs of Figs. 7, 8, and 9. These enable a comparison to be made of the values for I.T.E. determined when using pentane, hexane, and heptane in the running conditions required for nuclear ignition, with those determined when using benzene with similar values of C.R. and M.S. and with ignition necessarily by spark. The graphs of the three figures are lettered similarly and the references below will be made accordingly.

The A graphs, for the relation between C.R. and M.S., are of the W form always obtained when the paraffins are used in the conditions required for nuclear ignition. It differs characteristically from the U form obtained for benzene, with spark ignition even at relatively high values of C.R., as shown by graph A of Fig. 5.

The B graphs are for values of I.T.E. as determined for the paraffins when used at the values of M.S. and C.R. shown by the A graphs.

The C graphs are for values of I.T.E. determined when benzene was used at the values of C.R. and M.S. shown by the A graphs. The data for the C graphs

were obtained from the family of graphs, Fig. 4, and are extended into the weak mixture region, only until misfiring began.

It is to be remembered that the values given for benzene were determined in the higher heat load conditions in which an approach to a constant volume cycle was obtained for values of M.S. in the neighborhood of correct, and that the value of I.T.E. for any particular M.S. and the corresponding C.R., as taken from the graphs of Fig. 4, was always determined with optimum spark

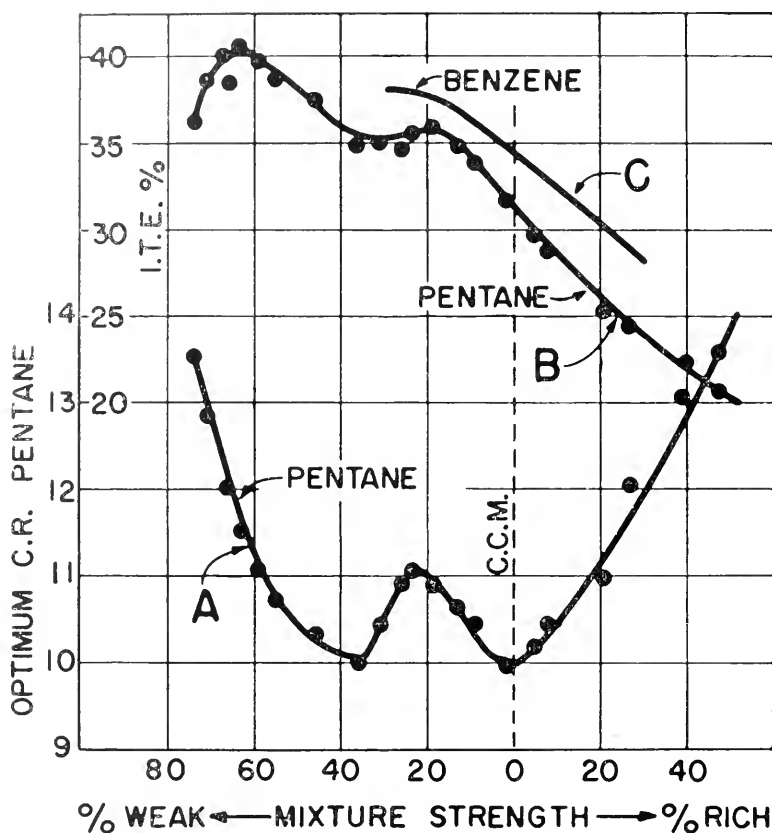


FIG. 7. Comparable values of I.T.E. Pentane with nuclear ignition. Benzene with spark ignition.

timing. The data for the paraffins were obtained when using compression ratios required for nuclear ignition with values always adjusted for maximum power output, that is, to an optimum. The heat of combustion was always added, in the circumstances, to the working fluid at constant volume as illustrated by the indicator diagrams of Fig. 1.

The values for I.T.E. obtained in the circumstances were always lower for the paraffins than for benzene, as shown by the B and C graphs of Figs. 7, 8, and 9. The percentages by which they were lower were 7% for pentane and hexane and 8% for heptane when M.S. was 20% weak. At correct mixtures, I.T.E. for the three paraffins was approximately 10% lower than for benzene.

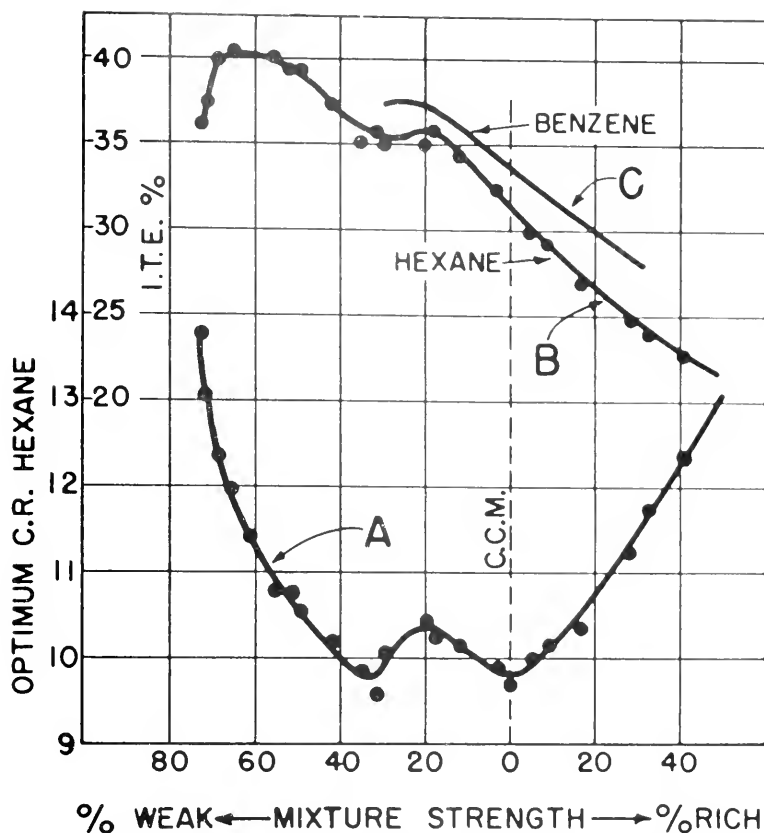


FIG. 8. Comparable values of I.T.E. Hexane with nuclear ignition. Benzene with spark ignition.

The extent to which relative values for I.T.E. were affected by the changes in running conditions that were required to obtain an approach to a constant volume cycle when using benzene may require some consideration.

The most important change was the increase in speed from 100 to 900 r.p.m. The effect on I.T.E. as measured over a higher speed range has been investigated by Ricardo for liquid fuels when used with spark ignition, and found to be negligible, as discussed by Pye (10, p. 205).

When using a paraffin with ignition by *compression* the increase of speed from 400 to 900 r.p.m. would, according to the nuclear theory, have the effect of extending two stage ignition into mixtures richer than 20% weak, with the consequence that I.T.E. for these would be lower than was determined at 400 r.p.m.

The jacket coolant was maintained at 100° F. for the experiments with the paraffins and at 140° F. for those with benzene. It was shown by experiments with town gas, described in Part XII of this series of papers, that the effect on I.T.E. of increasing the jacket coolant by 72° F. was nil. A larger increase of 211° F. led to a decrease of 2.5%.

The increase in the temperature of the air supply of from 50° F. to 140° F. for the benzene experiments would raise the temperature of the cycle and consequently be of adverse effect on thermal efficiency.

The increase in I.T.E. obtained on increasing charge density to "normal", when using a paraffin fuel, is discussed in Section VI and shown by the graphs of Fig. 10. An increase occurred when using the weak mixtures in which ignition and combustion occurred in two stages. These mixtures were leaner than any benzene-air mixtures that could be ignited by an electric spark and it was concluded that I.T.E. for benzene was not affected by charge density over the range of mixture strength ignitable by spark.

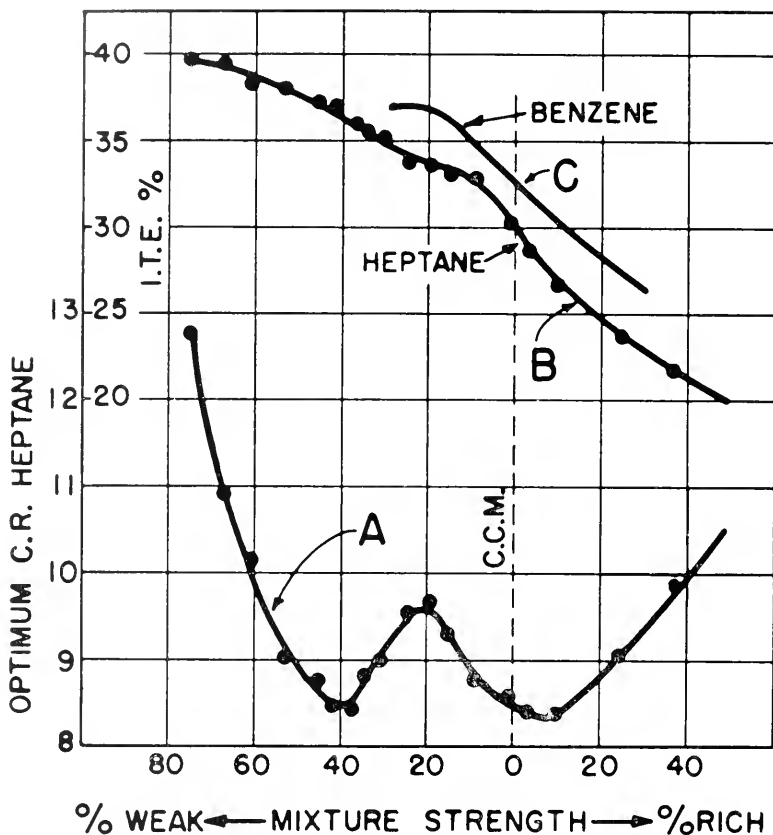


FIG. 9. Comparable values of I.T.E. Heptane with nuclear ignition. Benzene with spark ignition.

V. RESIDUAL PRODUCTS OF THE DECOMPOSITION OF PARAFFIN FUELS

It is shown by the diagrams of Fig. 1 that nuclear ignition of the paraffins used for the experiments occurs in a single stage with mixtures richer than approximately 20% weak. The quantity of very finely divided carbon derived

from the cracking of the paraffin would depend on charge density, M.S., C.R., engine speed, and the stability of the fuel molecules. As it would exist in a finely divided state, it would tend to be burned in the flame or to be carried out of the combustion chamber during the exhaust stroke. The amount of deposit remaining in the combustion chamber would then depend mainly on its retention by a film of lubricating oil.

When heptane was used as a fuel, with a charge density of 78% of normal, scattered particles of carbon appeared on the piston crown and patches of carbon on the blind plugs when M.S. was increased to be 20% weak. This was after the engine had run on still weaker mixtures and a brown color had been obtained only on the surfaces mentioned. On further increasing M.S. to the correct value, a very thin and patchy layer of carbon was seen on the piston crown and a nearly uniform layer on the cooler surfaces of the blind plugs. A further increase in the carbon residue was observed when over-rich mixtures were used, Part XXI (6, p. 215).

Observations of carbon residues made recently but with the lower charge density of 64% of normal disclosed that as before, carbon deposits on the piston crown became just visible with mixtures 20% weak, but there was little increase in their density as mixture strength was increased, C.R. always being adjusted to maintain maximum power output.

The engine was used recently for a series of experiments with extremely weak heptane-air mixtures extending over a period of several weeks. Consistent experimental results then ceased to be obtained and the engine was dismantled for inspection. All water cooled surfaces were found to be coated with globules of a resin-like substance varying in size to a maximum of about 1/64 in. in diameter. A similar deposit, but extremely thin, was found on the inlet valve. There was no deposit on the exhaust valve. These deposits could be wiped off easily. The deposits varied in color. They were dark brown on the water cooled surfaces, including the inner ends of the blank spark plugs. There was a similar color on the rim of the piston crown but it tended to turn reddish brown and then to a purplish brown as the center was approached. The deposits not exposed directly to flame tended to build up and become black and gummy. Those on uncovered screw threads of spark plug holes which were not sealed by the unthreaded ends of the blank spark plugs became so hard that a spark plug tap was required for their removal.

A black, very gummy deposit was found on the lands between piston rings and on the faces of the second and third compression rings which had become stuck in their grooves. The oil scraper ring had remained in good operating condition. All grooves of the compression rings were filled with the black gummy deposit. This had hardened to such an extent that the second and third rings could not be removed without being broken. It appeared that the deposits found below the crown of the piston were similar initially to those found in the combustion chamber but that they had become mixed with decomposed lubricating oil and had tended to accumulate and harden when not exposed to oxidizing conditions.

It is well known that aldehyde especially is a product of the combustion of weak mixtures in diesel engines and Webber (13), when discussing methods of maintaining pistons and rings in clean condition, mentions that synthetic resins formed from the aldehyde provide the binding for carbonaceous deposits.

VI. DISCUSSION

Reactions Prior to Ignition

Oxidation or decomposition reactions may occur prior to spark ignition in a carburetor engine, and experiments by others have been carried out in conditions such that oxidation reactions predominate. Thus jackets have been maintained at relatively high temperatures and heat added to the fuel-air mixtures in an attempt to reproduce the temperature conditions of maximum power output at the relatively low compression ratios required to avoid detonation when spark ignition is used. In these circumstances aldehyde is the first oxidation product formed in measurable quantity and its formation is accompanied by a minute proportion of peroxide. The peroxide has been assumed to be responsible in one way or another for the autoignition and the consequent "detonation" obtained on raising the compression ratio when fuels subject to that phenomenon are used. A "motored" engine without spark ignition is used frequently for these experiments.

It appears that Callendar and associates (1, pp. 27-28), 1926, were the first to use a motored engine to demonstrate the formation of aldehydes and peroxides in the temperature condition mentioned. Improved methods of experiment were used by Egerton and associates (2), 1935, in that by means of a sampling valve, the increase in the rates of formation of aldehyde and peroxide during compression were determined while the engine was developing power.

There was little if any publication of results of similar investigations until in recent years the possible effect of preflame reactions on the velocity of combustion in other than piston engines became of interest. Preflame reactions can however be studied most conveniently when using piston engines. Experiments made accordingly, but in temperature conditions suitable for the promotion of oxidation reactions, have been described recently by Retailliau, Ricards, and Jones (11), by Levedahl and Howard (8), and by Pastell (9). It is mentioned by Pastell that the form of the graph, Fig. 4, of his paper may be due to endothermic cracking reactions.

Method Used During Compression to Promote Decomposition Reactions Only

The method was devised to avoid surface oxidation of the fuel during compression and to make possible the use of paraffin fuels at compression ratios such that the temperatures and pressures attained by the end of compression would approach those of the end gas with ignition by spark. Autoignition would then, at a suitable high compression ratio, be initiated in some part of the whole charge instead of in some part of the end gas only.

Oxidation was avoided by the use of operating conditions required for an

exceptionally low heat load as described in Section I. The surface in the combustion chamber which, in the absence of a spark plug, would attain the maximum temperature was that of the exhaust valve. Its mean temperature was shown by separate experiments to be approximately 625° F. (329° C.) when the engine was running on autoignition, a correct heptane-air mixture, and the C.R. required for maximum power output. The temperature fell rapidly to 330° F. (165° C.) approximately as M.S. was reduced to 20% weak. The low heat load of the experiments was due in part to a reduction of charge density, generally to 64% of normal. This, in addition, had the effect of reducing the pressure due to autoignition to an extent that could be tolerated by the engine. Thus it was possible to measure the indicated thermal efficiency corresponding to the maximum power output for any ignitable mixture and to compare the values with those obtained when using a fuel such as benzene which did not decompose in the engine to provide material nuclei of ignition.

The Adverse Effect of Decomposition on Thermal Efficiency

The heat of compression would be insufficient, on the basis of published values for the "energy of activation", to decompose the whole of the fuel in a mixture even 20% weak to the extent required to produce finely divided carbon as nuclei of ignition. The values were obtained for vapors unmixed with air, contained in glass reactors, externally heated. They may not apply to engine conditions in which the vapor is mixed with air and heated rapidly by compression. It may however safely be assumed, in the absence of relevant data, that, as stated in Part XX (I, p. 39), decomposition of the fuel to the extent necessary to produce nuclei of ignition would occur in the part of the charge which had attained a higher than average temperature. That would be the part adjacent to the hot exhaust valve. It is not yet clear whether the rapid combustion which follows the nuclear ignition of this part of the charge is due to the consequent pressure wave or to a thermal process initiated by a relatively large volume of flame. The process of the nuclear ignition and subsequent combustion of the charge occurred in approximately 3° of crank revolution when a correct heptane-air mixture was used at a C.R. of 8.5, Fig. 1. That would be in 0.00125 sec., and a comparison of the values of I.T.E. obtained accordingly with those for the relatively slow burning benzene presents some difficulty. Thus we obtained a value of 31% for I.T.E., when using a correct benzene-air mixture at a C.R. of 7.0, and a heat load such that preignition did not occur (5, p. 33). Ricardo, using a heat load estimated to have been 40% greater, obtained 37% for the I.T.E. at a C.R. of 6.9, but could not use a higher value because of the onset of preignition (12, pp. 111-115). Furthermore it will be seen by reference to Fig. 6 that an increase of heat load from a relatively low value to the maximum used for the experiments with benzene described in this Part led to an increase in I.T.E. of from 29.5 to 35% at a C.R. of 10. This increase was shown by experiment to be due to the heat of combustion of the benzene having been added to the working fluid at more nearly constant volume. It is to be noted here that the increase occurred in spite of the decrease that would be expected because of the higher temperature

of the cycle. The heat of combustion of the paraffin is shown by the indicator diagrams of Fig. 1 to have been added to the working fluid at constant volume for mixtures within the range correct to 20% weak. It may be concluded therefore that higher values for I.T.E. than those observed would have been obtained for benzene-air mixtures if it had been possible to use a higher heat load without the onset of preignition. The result would be that a greater adverse effect on thermal efficiency than that observed could then be attributed to the heat absorbed by the decomposition reaction required for the nuclear ignition of the paraffin-air mixtures. This, as shown by the B and C graphs of Figs. 7, 8, and 9, accounted for the values of I.T.E. for the paraffins being from 7 to 10% lower than those for benzene, in similar conditions of M.S. and C.R.

The Nuclear Theory of Ignition

The theory was developed, as described in Part IV (3), to account for the autoignition of the end gas in spark ignition carburetor engines. It was therefore applied only to fuel-air mixtures richer than 20% weak because spark ignition tends to be ineffective as mixture strength is further reduced. Autoignition with mixtures richer than 20% weak was attributed, according to the theory, to the igniting effect of finely divided carbon derived from the cracking of the fuel at the temperature and pressures attained by the end gas, and residues of the carbon always appeared on the piston crown.

It is significant that, when using mixtures leaner than 20% weak, formaldehyde was detectable in the exhaust and residues of a resinous nature appeared on the piston crown, Part XXI (6, pp. 246-247), and that, after a long period of running on weak mixtures, residues which appeared to be a mixture of resins and carbon had the effect of sticking piston rings firmly in their grooves, Section V.

The surfaces in the combustion chamber of the C.F.R.-F2 engine do not attain temperatures required for the oxidation of the paraffins to aldehyde in the low heat load conditions of the experiments even when correct mixtures are used. This statement is based on temperature measurements which will be described in a subsequent Part. However, on decreasing M.S. and raising C.R. to maintain optimum power output, there is a further decrease in heat load, which depends mainly on the heat of combustion; thus surface temperatures decrease while the temperature of the charge increases. The aldehyde always present in the products of the combustion of weak mixtures must then have been formed on the carbon nuclei present in the charge as a result of the cracking of the paraffin. The compressed mixture may then contain nuclei of finely divided carbon and nuclei composed of a mixture of resins and carbon, which differ in degree of inflammability. This difference affords an explanation for the occurrence of two-stage ignition in mixtures leaner than 20% weak, in the conditions of the experiments described in this Part.

This extension of the nuclear theory of ignition, although regarded at present as a working hypothesis, appears to afford an explanation for the characteristics of the two-stage ignition of mixtures leaner than 20% weak.

Nuclear Ignition and the Lower Limit of Inflammability

The indicator diagrams of Fig. 1 show that the nuclear ignition of heptane, taken as a typical paraffin, occurred in a single stage when mixtures with air richer than 20% weak were used. It is indicated by experiments described earlier that the nuclei of ignition were those of finely divided carbon. Ignition began to occur in two stages when weaker mixtures were used. It will be seen by reference to the graphs of Figs. 7 to 9 that this double igniting effect continued to be effective until the paraffin-air mixtures were from 70 to 80% weak. This was not the limit. In other experiments, Part XXI (6, p. 214) with heptane as the fuel, nuclear ignition continued, as C.R. was always raised to an optimum value as M.S. was diminished until it became 93% weak. The air-fuel ratio was then 220 : 1 by weight and the Opt. C.R. 22.8. The power developed was not sufficient to run the engine at the speed of the experiments, 400 r.p.m., and the deficiency in power was supplied from the dynamometer used as a motor. Heptane was used for these experiments because it decomposes more readily than hexane or pentane to supply nuclei of ignition.

The experimental results show that the enormous extension of the lower limit of inflammability of the paraffin-air mixtures was not due fundamentally to the high temperatures and pressures attained on increasing C.R. Thus it occurred solely when using the fuels which could be decomposed to provide material nuclei.

Characteristics of Two Stage Nuclear Ignition; Mixtures Leaner Than 20% Weak

The mixture range 20 to 40% weak was marked by the advent of two-stage ignition, the occurrence of formaldehyde in the exhaust, the appearance of residues of combustion which appeared to be mixtures of resins and carbon, a decrease in the C.R. required to maintain optimum power output, and a tendency for I.T.E. to remain constant. A nearly constant value was obtained when using hexane and pentane and an approach to such a value when using heptane, see Fig. 3. The nearly constant value for I.T.E. can be accounted for, as mentioned earlier, by the increase due to decreasing M.S. being offset by the decrease due to decreasing values of Opt. C.R. The decrease in Opt. C.R. is attributed, according to the extension of the nuclear theory, to the compressed charge containing two types of nuclei, namely, those of finely divided carbon and others consisting of mixtures of carbon and resins. The latter being the more inflammable would initiate a first stage of ignition which would cause and be followed immediately by a second stage depending on the less inflammable nuclei of finely divided carbon.

The increase of C.R. required to maintain optimum power output when using mixtures leaner than 40% weak is regarded as being required to maintain a necessary first stage of ignition. The first stage, on this basis, must be considered as a "primer" for the second stage.

The values of I.T.E. for mixtures leaner than 40% weak rose slowly in relation to the increase of C.R. required to maintain optimum power output. A maximum value of 40% for I.T.E. was obtained when mixtures were 65%

weak. There was then a rapid decrease in I.T.E. as mixtures leaner than 65% weak were used, although C.R. was raised rapidly in order to maintain an optimum value. Thus I.T.E. had fallen to 34% and Opt. C.R. had risen to 15.5 when the mixture became 80% weak.

The relatively low values for maximum I.T.E. obtained in the low heat load conditions of the experiments can be explained as follows: The heat due to combustion of the fuel decreases proportionally to the decrease in M.S., with the consequence that the mean temperatures of the surfaces in the combustion chamber decrease and an increasing proportion of the heat of compression is absorbed by them. An abnormal increase in Opt. C.R. is then required to raise the temperature of the gaseous charge to that required for decomposition of the paraffin to the extent required for the provision of nuclei of ignition. The *quantity* of heat available during compression can however be increased by increasing charge density, without increasing the temperature, if compression ratio remains unchanged. Thus an increased proportion of the

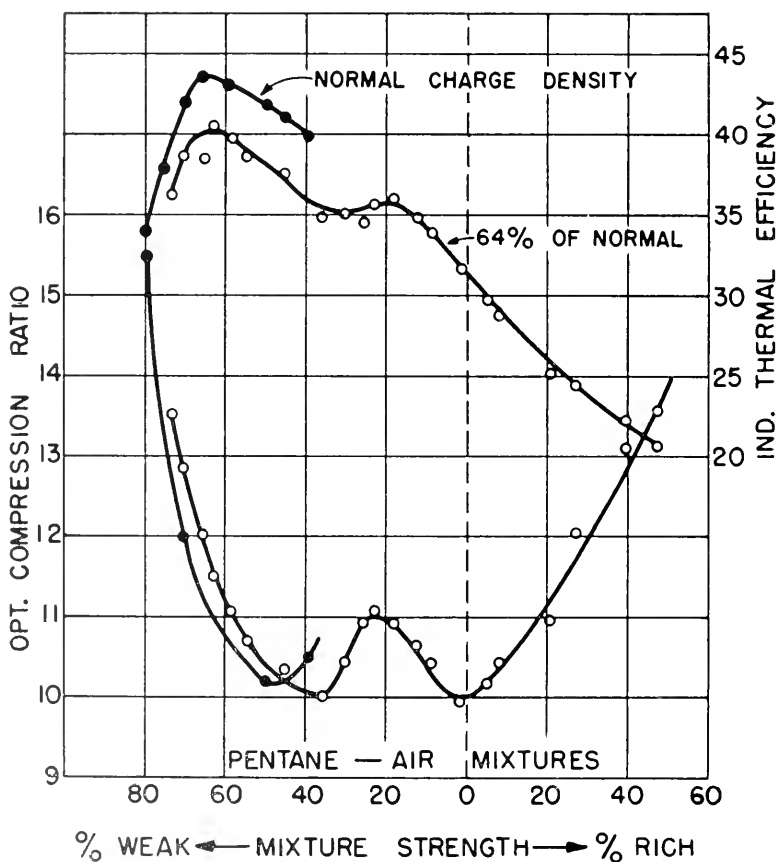


FIG. 10. Effect of increase of charge density to increase I.T.E.
 ● Normal charge density.
 ○ 64% of normal.

heat of compression would be available for the decomposition reaction and for conversion into power with a corresponding increase in I.T.E.

An experiment was tried accordingly with a charge density of "normal", obtained by using the standard C.F.R. carburetor fitted with a 9/16 in. diameter venturi instead of the choke tube used to obtain 61% of normal charge density. It is estimated that an increase of charge density of 33% was obtained. The other running conditions were not changed, that is, engine speed was maintained at 400 r.p.m., the jacket coolant at 100° F., and the air supply at 50° F. Beginning with a mixture 80% weak, it could be increased to 40% weak before the occurrence of an intolerable intensity of knocking combustion. The results of the experiments are exhibited by the graphs of Fig. 10. They show that maximum I.T.E. increased by approximately 9% on increasing the charge density while the corresponding Opt. C.R. decreased from 11.7 to 11.1, and it appears that with the greater available quantity of heat, the increase of I.T.E. was obtained with a lower compression temperature.

CONCLUSION

The method used for the experiments with the paraffins has made possible the investigation of the gas phase reactions required for ignition by compression and the nature of these as affected by mixture strength. The experimental work is regarded as being of a preliminary nature. Further data relating to two-stage ignition, surface temperatures, and the mechanism of decomposition of fuels in engine conditions are required for a more complete understanding of the fundamentals of combustion as it occurs in engines.

ACKNOWLEDGMENTS

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THE OXIDATION, DECOMPOSITION, IGNITION, AND DETONATION OF FUEL VAPORS AND GASES

XXV. THE TRANSITION FROM SPARK TO NUCLEAR IGNITION AS COMPRESSION RATIO IS RAISED¹

By R. O. KING² AND A. B. ALLAN³

ABSTRACT

An experimental study of the characteristics of combustion during the transition from spark to nuclear ignition as compression ratio is raised is described in this Part. Heptane was used as the fuel for a C.F.R. engine operated at 400 r.p.m. Compression ratio was always adjusted for maximum power output as the mixture with air was varied from 65% weak to 25% rich. Charge densities of 64 and 78% of normal were used. The progressive changes in the relation between compression ratio and mixture strength and between thermal efficiency and mixture strength are shown by families of graphs. Pressure-time indicator diagrams are used to illustrate the changes that occur in the mean values of pressure during the transition from spark to nuclear ignition. Rate of pressure change diagrams taken simultaneously with a dual beam oscilloscope show the high frequency pressure vibrations due to the nuclear ignition of the part of the compressed charge adjacent to the combustion chamber surface of maximum temperature.

INTRODUCTION

A transition from spark to nuclear ignition can be obtained on increasing compression ratio if fuels are used which decompose (crack) in a manner to form material nuclei. The changes in the relation between thermal efficiency and compression ratio as the transition occurs cannot be determined in the usual conditions of engine operation because of the accompanying severity of knocking combustion commonly described as detonation. Nuclear ignition does not however occur simultaneously throughout the mass of the charge in an engine but begins in some part where the temperature and mixture conditions are such that decomposition can occur. In these circumstances the combustion knock due to the consequent pressure waves can be tolerated by the C.F.R. engine if charge density be reduced by approximately 20%. The relation between thermal efficiency and compression ratio can then be determined even when the engine is operated at the relatively low speed of 400 r.p.m., the heat of combustion added to the working fluid substantially at constant volume, and a correct mixture used. Then if the jacket coolant and the air supply be maintained at relatively low temperatures, surfaces in the combustion chamber do not attain temperatures required for oxidation of the fuel during compression and decomposition becomes the sole prellame reaction.

Experiments made accordingly with pentane, hexane, and heptane as engine fuels for the C.F.R. engine are described in Part XXI (5). It was indicated

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by these experiments that nuclear ignition started in the part of the charge adjacent to the ceramic core of an unfired spark plug or, if the plug were removed, in the part adjacent to the exhaust valve.

The timing of nuclear ignition could always be regulated to obtain maximum power output by adjustment of compression ratio. The experiments were devoted mainly to showing that the relation between mixture strength and the compression ratio required for maximum power output, that is the optimum value, was represented by a graph of a W form instead of by the familiar U form obtained with spark ignition only.

It was found in the course of further experiments that sufficient time had not always been allowed between changes of mixture strength and compression ratio for the attainment of equilibrium temperatures by surfaces in the combustion chamber. Especial care was therefore taken when the experiments with heptane-air mixtures were carried out, as described in this Part, to run the engine at particular values of mixture strength until repeatable values were obtained for power output with the compression ratio adjusted to the optimum value. It is considered that reliable results were then obtained for the changes in the relation between thermal efficiency and compression ratio that occur during the transition from spark to nuclear ignition, as compression ratio is raised. Series of experiments were carried out with charge densities of 64 and 78% of normal.

EXPERIMENTAL CONDITIONS

The experimental arrangements and conditions were similar to those described in some detail in Part XIX (4, pp. 30-32, 33). The essential conditions were,—

air supply 50°F.; jacket coolant 95°F. at inlet, 100°F. at outlet; engine speed 400 r.p.m.; unshrouded inlet valve.

Charge densities of 64 and 78% of normal were obtained by fitting long choke tubes of suitable diameter into the standard C.F.R. carburetor. The tubes were curved to discharge into the well of the inlet valve, see Part XIX (4, p. 40).

Experiments were carried out at each of the subnormal charge densities with ignition by spark at 20°, 15°, 10°, and 5° in advance of t.d.c. with no spark, and with the spark plug replaced by a blank steel plug.

There were three spark plug holes in the wall of the cylinder of the C.F.R. engine. A C.F.R.-8 spark plug, which is a hot variety, was used in the standard position for experiments with spark ignition. The two other holes were fitted with blank plugs or used for pressure pickups when indicator diagrams were taken. The bouncing pin hole in the cylinder head was always fitted with a blank plug.

The fuel used for the experiments was the normal heptane supplied by Phillips Petroleum Company and approved by the A.S.T.M. as a reference fuel for knock rating. Calculations of thermal efficiency were based on the heptane having a lower calorific value of 19160 B.T.U./lb.

The abbreviations Opt. C.R., I.T.E., and M.S. are used in subsequent text for Optimum Compression Ratio, Indicated Thermal Efficiency, and Mixture Strength, respectively.

I. EXPERIMENTAL RESULTS: CHARGE DENSITY 64% OF NORMAL

Experimental results are given by the graphs of Fig. 1 for the relation between Opt. C.R. and M.S. and between I.T.E. and M.S.

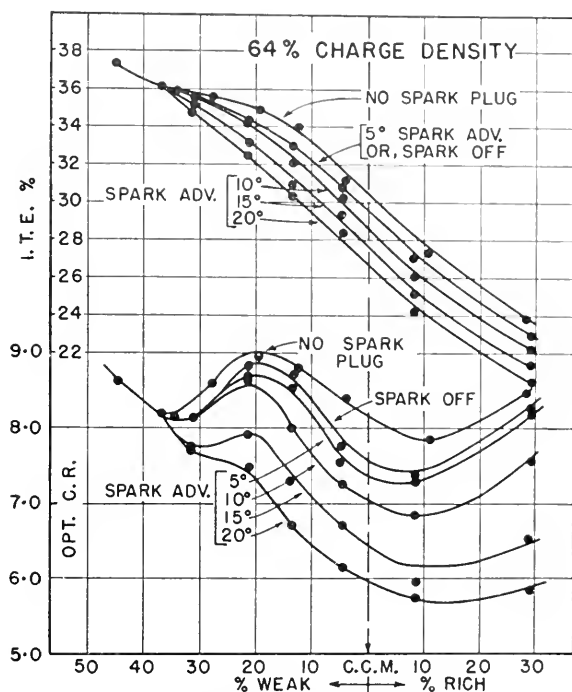


FIG. 1. Upper graphs, relation between I.T.E. and M.S.; lower graphs, relation between Opt. C.R. and M.S. Charge density, 64% of normal.

There was some degree of detonation with a spark advance of 20° when the mixtures were nearly correct or richer. Knock intensity increased as spark timing was retarded and Opt. C.R. increased accordingly. Repeatable values were obtainable for Opt. C.R. until spark advance was reduced to 5°. Ignition then tended to become independent of the spark and when C.R. was raised to the Optimum value ignition soon became of the runaway type characteristic of preignition and was accompanied by severe knock. Although the values thus obtained for Opt. C.R. with the spark off were somewhat higher than with it on, the differences in the corresponding values of I.T.E. were inappreciable. The relation between I.T.E. and M.S. is therefore given by a single graph.

When the spark plug was replaced by a blank plug, the higher values then required for Opt. C.R. remained substantially constant irrespective of time of

running. There was a slight degree of knock when a mixture 40% weak was used. Knock intensity increased as M.S. was increased and became medium heavy over the mixture range 20 to 15% weak. Intensity attained a maximum with mixtures within the M.S. range correct to 10% rich. It is of interest that with nuclear ignition, knock intensity varied with mixture strength, not with compression ratio. Thus the value of Opt. C.R. was 8.5 for mixtures 43% weak, 30% weak, 7.5% weak, and 30% rich although over this range of M.S. knock intensity varied from very light to very severe.

Spark ignition remained effective as timing was retarded from 20° to 10° in advance of t.d.c. and partially so as timing was further retarded to 5° advance, over the mixture range 25% rich to 25 or 30% weak. Within this range it was necessary to *raise* the C.R. to obtain an optimum value as M.S. was reduced from approximately 10% rich or as it was increased from that value and it will be seen by reference to Fig. 1 that the graphs for the relation between Opt. C.R. and M.S. were then of the conventional U shape.

As M.S. was reduced to be leaner than 25 to 30% weak, spark ignition became progressively ineffective until it failed completely when the mixture was 40% weak. Over this mixture strength range of failing spark ignition it was necessary to lower C.R. progressively in order to maintain an optimum value.

The transition from spark to nuclear ignition having been completed on reducing M.S. to be 40% weak, the engine continued to run on nuclear ignition only as M.S. was further reduced. It was then necessary to raise C.R. progressively in order to maintain an optimum value. A symmetrical W form was then obtained for the graph relating I.T.E. and C.R. with mixtures ranging from 45% weak to 50% rich.

The Relation Between I.T.E. and Opt. C.R.

It is now apparent that the graphs of Fig. 1, if plotted on a base of Opt. C.R. instead of M.S., will illustrate the transition from single to two stage ignition as well as the transition from spark to nuclear ignition. The series of graphs thus derived are shown by Fig. 2. The "points" on the graphs are for 5% changes of M.S. and the correct value is marked CCM.

The graphs move toward higher values of Opt. C.R. as spark timing is retarded from 20° to 5° in advance of t.d.c. and continue to do so as ignition is obtained without spark and with the spark plug replaced by a blank plug. In all of these ignition conditions the graphs for the relation between I.T.E. and Opt. C.R. are of the conventional form until M.S. is reduced to be approximately 20% weak, but the value of I.T.E. increased from a minimum of 32% with a spark advance of 20° to a maximum of 34.6% with nuclear ignition in the absence of a spark plug. The transition from single to two stage ignition then began and became complete on reducing M.S. to 40% weak. Then transition is indicated by a single inflection in the graph obtained with a spark advance of 20°. The beginning of a double inflection is shown by the graph obtained when the spark advance was 15°. The range of Opt. C.R. over which a double inflection occurred increased as spark timing was further retarded and succeeded by nuclear ignition. Finally when nuclear ignition

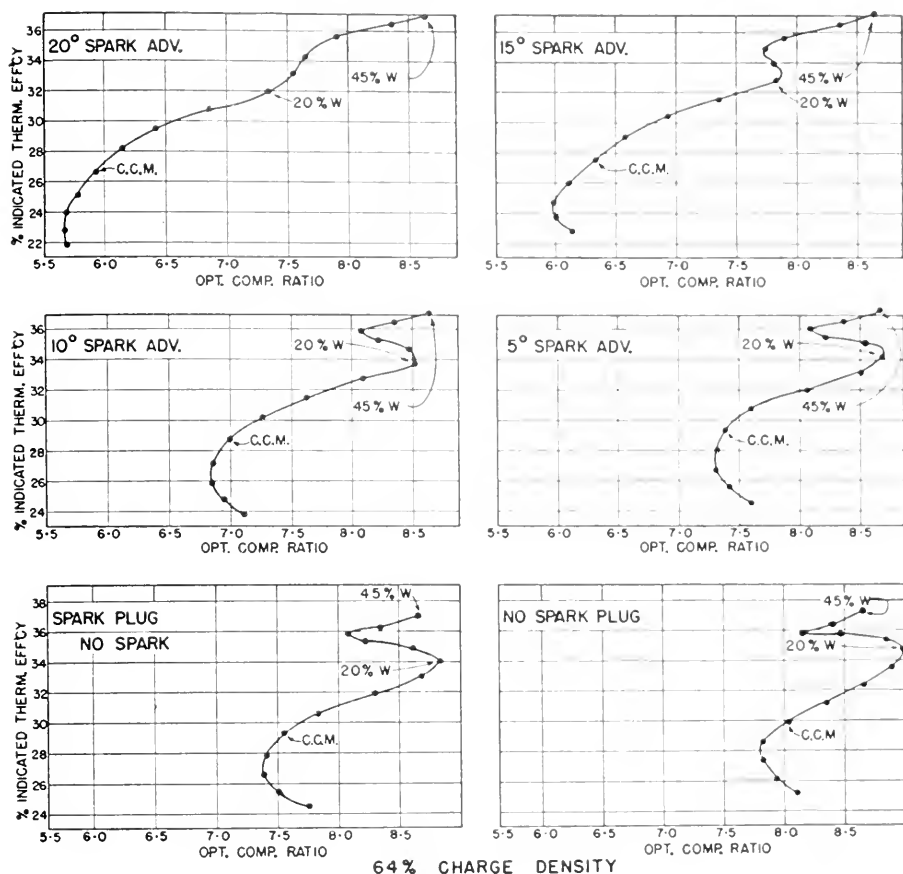


FIG. 2. Progressive change in the relation between I.T.E. and Opt. C.R. during the transition from spark to nuclear ignition. Charge density 64% of normal.

occurred in the absence of a spark plug, I.T.E. tended to become constant for values of Opt. C.R. *diminishing* from 9.0 to 8.4, while at the same time M.S. decreased from 25 to 40% weak. The explanation for this effect is as given in Part XXIV (3, p. 227), namely that as the transition from spark to nuclear ignition occurs, then as M.S. is reduced from 25 to 40% weak, the increase in I.T.E. to be expected is counteracted by the adverse effect on thermal efficiency of the heat absorbed by the endothermic reaction necessary for the provision of nuclei of ignition. It will be noted that after the transition to nuclear ignition is complete, at a M.S. of approximately 40% weak, I.T.E. increases as M.S. is further reduced and compression ratio raised to maintain an Optimum value.

II. EXPERIMENTAL RESULTS: CHARGE DENSITY 78% OF NORMAL

The experiments were carried farther into the weak mixture region than those of Section I. Results are given by the graphs of Fig. 3 for the relation

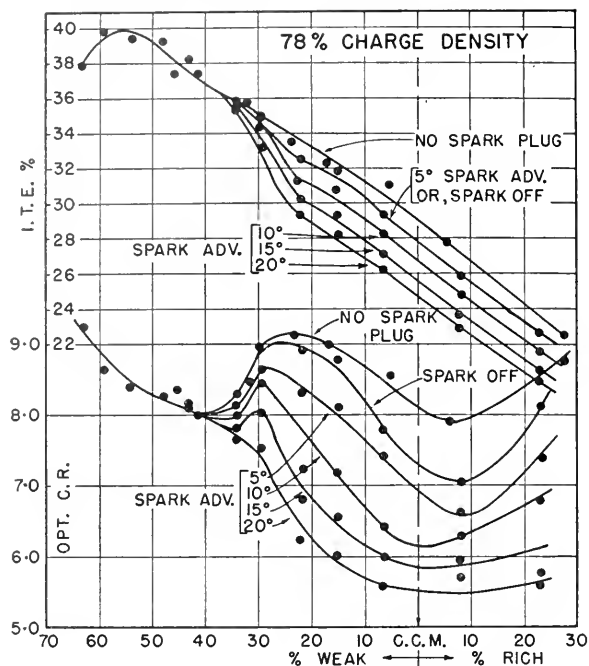


FIG. 3. Upper graphs, relation between I.T.E. and M.S.; lower graphs, relation between Opt. C.R. and M.S. Charge density, 78% of normal.

between C.R. and M.S. and between I.T.E. and M.S. They are similar in character to those obtained when a charge density of 64% of normal is used and the related description applies also to the results obtained with a charge density of 78% normal. The intensity of combustion knock at 78% charge density was the greater, as would be expected. It will be seen by reference to Fig. 3 that on decreasing M.S. to 65% weak I.T.E. passed through a maximum value of 40% for a mixture 55% weak.

The Change from Single to Two Stage Ignition

The series of graphs, Fig. 4, are similar to those of Fig. 2, and likewise illustrate the transition from spark to nuclear ignition as well as the transition from single to two stage ignition. The sole notable differences are that the transition from spark to nuclear ignition began with mixtures approximately 10% weaker than when the lower charge density was used and that the value of I.T.E. did not remain constant during the transition from spark to nuclear ignition but increased by one unit over the range of Opt. C.R. in which the transition occurred.

The Transition from Spark to Nuclear Ignition as Shown by Pressure-Time Indicator Diagrams

The diagrams, Fig. 5, were taken with spark timings of 20°, 15°, and 10°, and 5° before t.d.c., with no spark, and finally with the spark plug replaced by

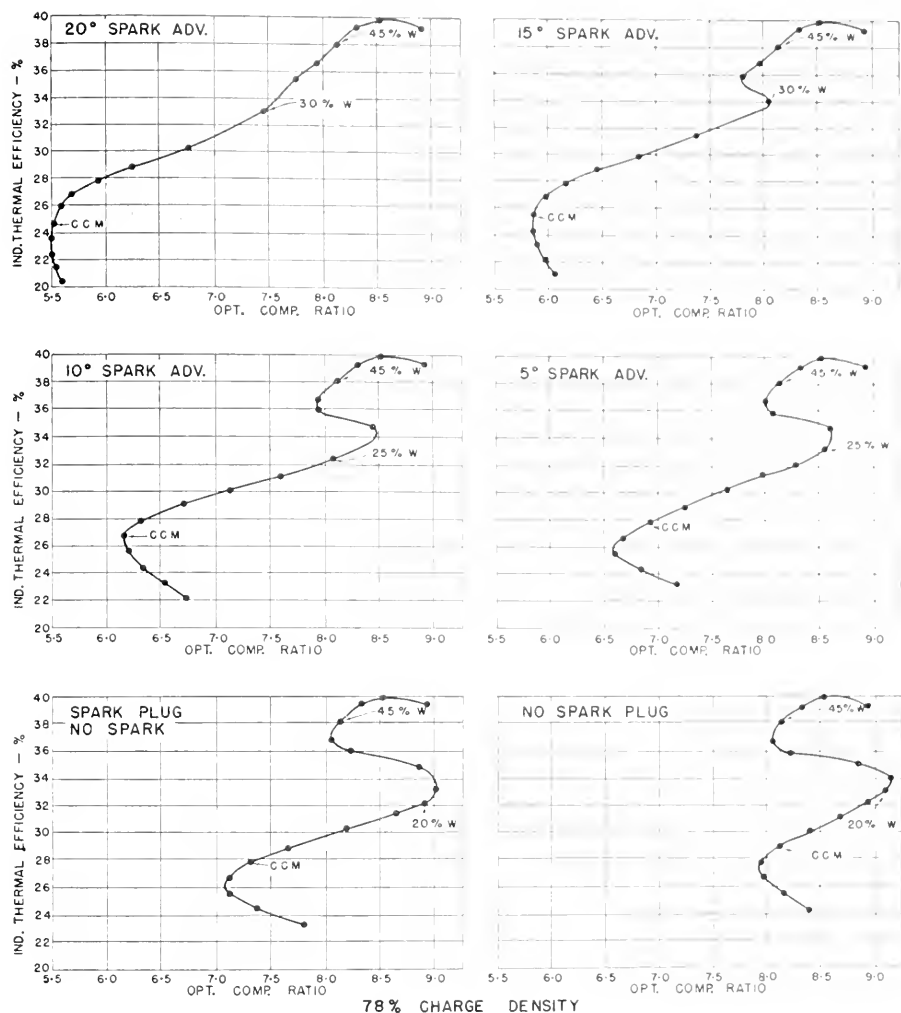


FIG. 4. Progressive change in the relation between I.T.E. and Opt. C.R. during the transition from spark to nuclear ignition. Charge density 78% of normal.

a steel blank. One series was taken with the heptane-air mixture 19% weak and another with a correct mixture. Reproductions of the diagrams are set out in the two vertical columns of Fig. 5. All were taken with C.R. adjusted for maximum power output. A "Sunbury" indicator was used for the experiments. The pressure scale is not linear, and a consequent effect is that, especially for the lower values of maximum combustion pressure, the expansion lines of the diagrams are nearly straight. The "blips" on the diagram occur at t.d.c. and at 10° of crank revolution for 30° before and after. The blip at t.d.c. is marked by a short vertical line. The blips on the upper and lower lines of the diagrams are out of step and spacing is somewhat irregular, because the inertia of

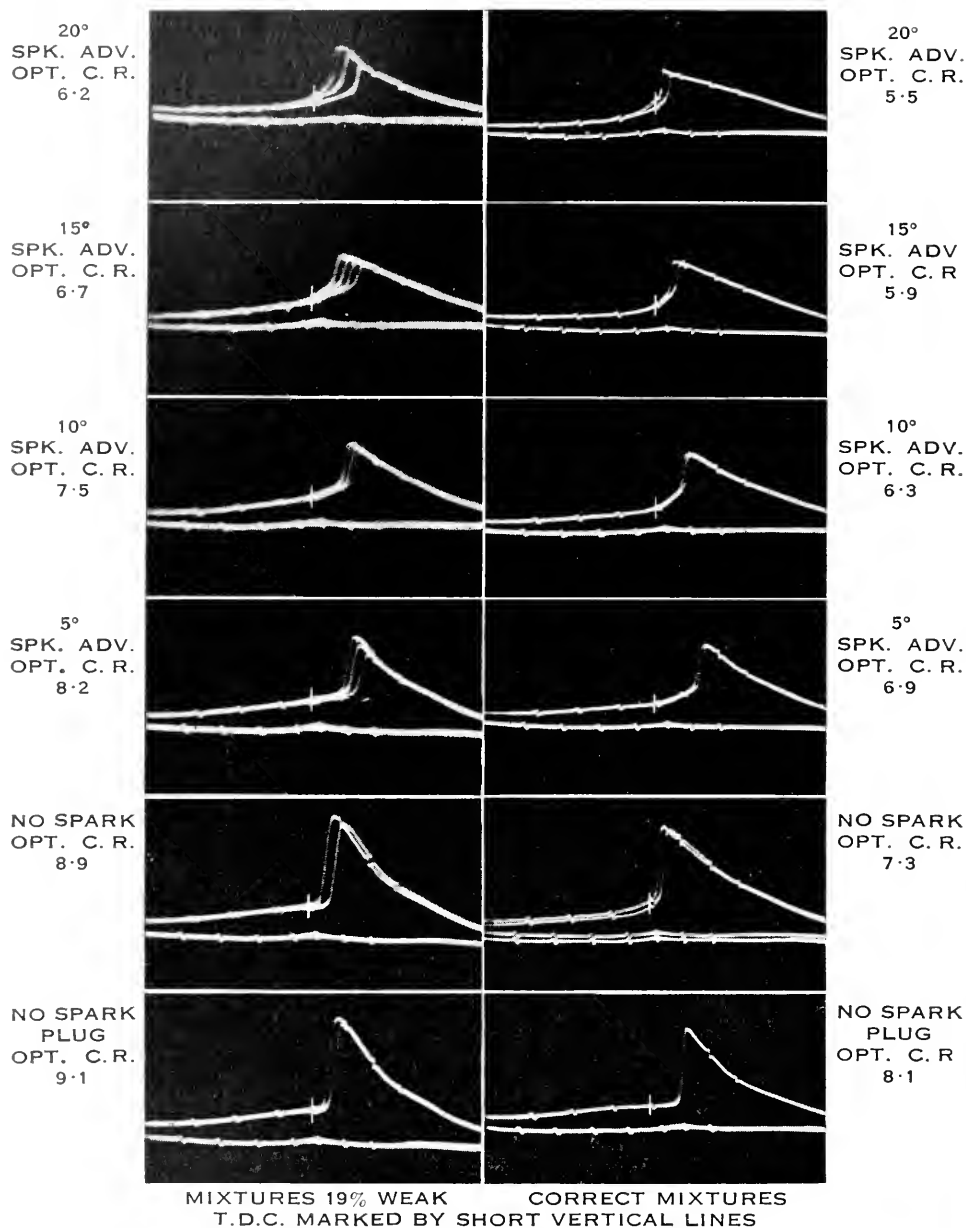


FIG. 5. Pressure-time diagrams. Charge density 78% of normal, transition from spark to nuclear ignition.

rotating parts of the C.F.R. unit is insufficient at the engine speed of 400 r.p.m. to damp out the effects of pressure changes in the cylinder.

The diagrams were taken when a charge density of 78% of normal was used. Values for Opt. C.R. and I.T.E. as given by Fig. 3 may therefore be used when comments are made on the corresponding combustion characteristics.

Diagrams for Mixtures 19% Weak

Starting with spark ignition 20° advance, Opt. C.R. was 6.2 and the diagram exhibits the irregularity of combustion commonly obtained when weak mixtures are ignited by spark. When spark ignition was retarded to 15° advance, Opt. C.R. increased to 6.7, combustion was more regular, and maximum combustion pressure was higher. When spark ignition was further retarded to 10° advance, a relatively large increase of C.R. to 7.5 was required in order to obtain maximum power output and the diagram shows that the consequent increase in the rate and magnitude of combustion pressure rise was accompanied by more regular combustion. Rate of pressure rise and maximum combustion pressure again increased when the spark was further retarded to 5° advance, and an increase of Opt. C.R. to 8.2 was required to maintain maximum power output. The engine would then run without spark ignition, but not indefinitely because of a continuing diminution of power output. The beginning of a complete transition from spark to nuclear ignition was thus indicated.

Continuous running without spark ignition required the relatively large increase of Opt. C.R. from 8.2 to 8.9. The related diagram shows that combustion pressure rise began at 2° to 5° after t.d.c. whereas, with the spark on, the rise began at from 12° to 15° after t.d.c. but varied from cycle to cycle. The last diagram of the series was taken after the spark plug was replaced with a mild steel blank plug. A small increase in Opt. C.R. of 8.9 to 9.1 was then required for continuous running with nuclear ignition. The diagram shows that combustion pressure rise began at 5° after t.d.c. with little variation of the position of maximum combustion pressure, which occurred at 8° after t.d.c. during the three cycles shown by the diagram.

The interval between t.d.c. and the crank angle position of maximum combustion pressure varied irregularly from 5° to 15° with spark timings of 20°, 15°, and 10° in advance of t.d.c. When however the spark plug was replaced by a mild steel blank, maximum combustion pressure occurred regularly at between 8° to 10° after t.d.c.

When ignition was by spark, 10° in advance of t.d.c., a C.R. of 7.5 was required for maximum power output. When the spark plug was removed and ignition became a nuclear effect entirely, it was necessary to raise the C.R. to 9.1 to obtain maximum power output. Then, although the heat of combustion was added to the working fluid the more nearly at constant volume with nuclear ignition, the increase in I.T.E. was from 31 to 33% only.

Diagrams for Correct Mixtures

The diaphragm of the Sunbury pressure pickup proved to be too thin for satisfactory use with the nuclear ignition of correct mixtures. One slightly

thicker was therefore fitted to the pickup and although amplification was increased to the limit of the indicator, the pressure scales of the diagrams for correct mixture differ little from those for mixtures 19% weak. Then because the indicated pressure increase is less than the real increase, the expansion lines of the diagrams tend to remain linear until ignition is a nuclear effect and relatively high values are obtained for maximum combustion pressure.

The diagrams taken with spark ignition, especially those with ignition timing 20° and 15° in advance of t.d.c., indicate a greater regularity of combustion than was obtained with mixtures 19% weak. The intervals in degrees of crank angle between t.d.c. and the attainment of maximum combustion pressure are more clearly defined. The interval is shown to have increased from 5° to 15° as spark timing was retarded from 20° to 5° in advance of t.d.c. That is, the time of burning had decreased from 25° to 20° of crank revolution on increasing Opt. C.R. from 5.5 to 6.9. When spark timing was 5° in advance of t.d.c. the Opt. C.R. was 6.9, then with ignition "off" an increase in Opt. C.R. of 0.30 only was required for complete transition to nuclear ignition. Burning of the mixture then occurred in approximately 2° of crank revolution. There was however an indication that nuclear ignition was accompanied by some degree of nuclear preignition. The spark plug was then replaced by a blank plug and preignition did not occur.

III. DISCUSSION

The transition from spark to nuclear ignition as compression ratio is raised was illustrated by experiments with heptane, hexane, and pentane described in Part XXI (5). These experiments formed part of a general survey of the characteristics of nuclear ignition and were therefore of a somewhat preliminary nature. The experiments of this Part were carried out with heptane only, in greater detail and with some improvement in method.

The indicator diagrams of Fig. 5, taken when heptane-air mixtures 19% weak and correct were used, show that after ignition was initiated by a spark, combustion pressure rose in the manner characteristic of a normal rate of flame propagation until a transition occurred to nuclear ignition. This was marked by a pressure rise so rapid that combustion pressure attained a maximum value in a further 2° of crank revolution.

The transition which thus occurred after spark ignition 20° in advance of t.d.c. of a mixture 21% weak is shown clearly by the pressure-time and rate of pressure change diagrams of Fig. 6. They were taken simultaneously during the use of a dual beam Dumont oscilloscope. Spark ignition was by a C.F.R.-8 plug in the standard position. The "Sunbury" electronic circuit with a magnetic flux pressure pickup was used for the rate of change diagram. A "Photocon" electronic circuit with an electrostatic pressure pickup was used for the pressure-time diagram. It was possible accordingly to restrict pressure indications to the nearly linear part of the pressure scale.

A compression ratio of 8 : 1 was required for maximum power output and a value of 32.2% was obtained for indicated thermal efficiency. Top dead center is marked on the pressure-time diagram by a short vertical line and the timing

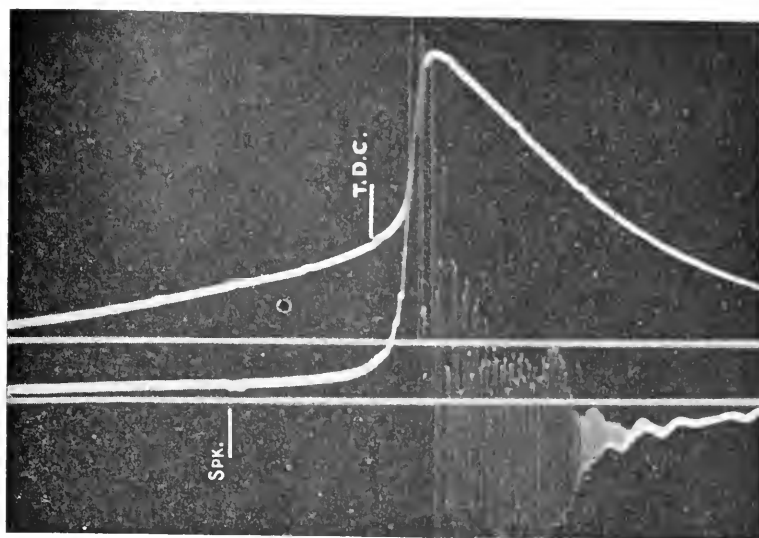


FIG. 6. Pressure-time and rate of change diagrams taken simultaneously; spark ignition 20° advance, followed by nuclear ignition. Mixture 21% weak, Opt. C.R. 8:1, I.T.E. 32.3%, speed 400 r.p.m. Charge density 64% of normal.

of the spark at 20° before t.d.c. is marked similarly on the rate of change diagram.

The pressure-time diagram is generally similar to those of Fig. 5, in that the gradual pressure rise following the spark ignition is succeeded by a sudden rise just prior to the attainment of maximum combustion pressure. This is attributed as before to the transition from spark to nuclear ignition. The pressure waves that necessarily accompanied nuclear ignition were, also as before, integrated to a mean value in the electronic circuit and do not show on the diagram. The approach of the expansion line to a true form is attributed to the use of superior indicating arrangements.

The diagram showing rate of change of pressure is of special interest. The rates of pressure change accompanying the pressure waves due to nuclear ignition are shown with exceptional clarity. Thus it will be seen that rate of change of pressure increased very slowly after spark ignition at 20° before t.d.c. until 5° before t.d.c. Rate of change then began to increase more rapidly as combustion continued in the normal manner without accompanying pressure waves. However after continuing for 10° of crank revolution, that is until 5° after t.d.c., explosive ignition occurred and the magnitude of the accompanying rate of pressure change was so great that it exceeded the pressure scale of the diagram. The high frequency pressure waves which followed explosive ignition are shown clearly by the accompanying rates of pressure change. They are attributed to reflections from surfaces and to the fact that nuclear ignition arose from more than a single source.

It is of interest that the process of combustion as illustrated by the rate of change diagram is in fair agreement with the knocking combustion that

followed spark ignition, as shown by the high speed photographs taken by Withrow and Rassweiler (6) and reproduced in Part IV (1).

Single Stage Nuclear Ignition

The characteristics of nuclear ignition when the consequent combustion occurred in a single stage are illustrated by the diagrams of Fig. 7. They were taken in the same operating condition and with the same mixture strength, namely 21% weak, but after the spark plug was replaced with a blank and the compression ratio was adjusted to the higher value of 9:1 then required for maximum power output without spark ignition.

The initiation of combustion without the aid of a spark required prior decomposition of the fuel to the extent necessary for the formation of an igniting concentration of nuclei in some part of the mixture with air, Part IV (1), Part XX (2, pp. 59-60). The occurrence of the decomposition reaction, which is endothermic, is indicated on the pressure-time diagram of Fig. 7 by the failure of pressure to rise during the final stage of compression and on the rate of change diagram by a zero value extending from t.d.c. to about 5° after. Small scale pressure waves are shown by that diagram to have then appeared early in the fillet joining compression pressure with combustion pressure. Combustion of the entire mixture then followed with such velocity that combustion pressure attained a maximum value in approximately 2° of crank revolution. The high frequency pressure waves which occurred during combustion are indicated by the rates of pressure change shown by the diagram and combustion appears to have been substantially completed before the beginning of expansion. In the absence of a spark or a spark plug core it

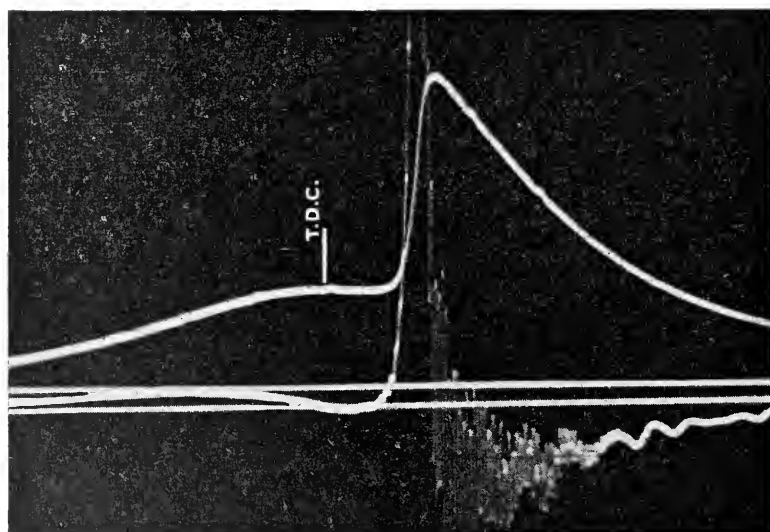


FIG. 7. Pressure-time and rate of change diagrams taken simultaneously; nuclear ignition only, mixture 21% weak, Opt. C.R. 9:1, I.T.E. 35.7%, speed 400 r.p.m. Charge density 64% of normal.

may be assumed that in the temperature conditions of the experiment, explosive nuclear ignition occurred in the part of the compressed mixture adjacent to the exhaust valve.

The heat of combustion was added to the working fluid more nearly at constant volume than when combustion of a similar mixture was initiated by a spark and completed with nuclear ignition. The consequent increase in thermal efficiency from 32.2% to 35.7% is greater than could be expected from the increase of Opt. C.R. from 8 to 9.1.

The rate of change diagrams show vibrations of relatively low frequency which become visible after expansion has proceeded for about 30° of crank revolution. These are due to mechanical vibration in the pressure pickup, set up by the prior explosive nuclear ignition.

Nuclear Ignition in One or Two Stages

The igniting effect has been shown by the experiments described in this Part to occur in a single stage for correct heptane air mixtures and for mixtures 19 and 21% weak, engine speed being 400 r.p.m. It was shown to occur in two stages at the same engine speed when the mixture was 70% weak, by experiments described in Part XXI (1, p. 230). Thus a transition from single to two stage nuclear ignition must occur within the mixture range 21 to 70% weak when heptane is used as the fuel and the engine speed is 400 r.p.m. The decomposition of the fuel to provide the concentration of nuclei required for ignition involves a time factor. It would be expected therefore that the transition from single to two stage nuclear ignition of a particular fuel would be affected by engine speed as well as by mixture strength. Thus it has been shown by experiments to be described in a subsequent Part that two stage nuclear ignition continues into mixtures even richer than correct, on increasing the engine speed to 600 r.p.m.

ACKNOWLEDGMENTS

The experiments described in this Part were carried out in the Department of Mechanical Engineering, University of Toronto, with the co-operation of Professor E. A. Allcut, Head of the Department, and the assistance of Mr. R. W. P. Anderson, Instructor in the Department. The investigation was sponsored by the Defence Research Board (Canada). The authors are indebted to the Board for permission to publish the results.

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THE OXIDATION, DECOMPOSITION, IGNITION, AND
DETONATION OF FUEL VAPORS AND GASES

XXVI. THE EFFECT OF FLOW CONFIGURATION ON THE OXIDATION AND
IGNITION OF HYDROGEN IN MIXTURES WITH AIR SUPPLIED TO
VERTICAL COMBUSTION TUBES OF VARIOUS MATERIALS

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XXVI. THE EFFECT OF FLOW CONFIGURATION ON THE OXIDATION AND IGNITION OF HYDROGEN IN MIXTURES WITH AIR SUPPLIED TO VERTICAL COMBUSTION TUBES OF VARIOUS MATERIALS¹

BY R. O. KING,² S. SANDLER,³ AND R. STROM⁴

ABSTRACT

Experiments to determine the effect of flow configuration on the oxidation and ignition of hydrogen in mixtures with air, described in this Part, are the second of a new series carried out with a method described in Part XXIII and used for experiments with acetaldehyde and pentane. Oxidation and ignition of hydrogen in mixtures with air occurred solely on the surface of the combustion tube. The wall temperature required for ignition, as measured on the outer surface, exceeded a minimum of 590°C. to an extent increasing with increases in hydrogen concentration, with increases in the catalytic activity of the tube surface, and with decreases in the rate of mixture supply if that rate were lower than the value required for turbulent flow. The effect of these factors depended to a remarkable degree on whether flow configuration was due to the convection circulations which existed at relatively low rates of mixture supply or to the turbulence accompanying greatly increased rates. When, for example, a mixture containing 50% of hydrogen was supplied to combustion tubes of silica and of stainless steel with an aged surface, at 200 cc./min. the surface temperatures required for ignition were 600° and 790°C. respectively. When, however, the rate of supply was increased to 1000 cc./min. and flow configuration became turbulent, ignition temperatures were in the same order but the total difference was 30°C. and diminished to approximately 15°C. only, as rate of mixture supply was further increased to 2500 cc./min. The increase in ignition temperatures, as measured on the outer surface of the combustion tubes, that always occurred after turbulence had been established and rate of mixture supply further increased was probably due to the increase in the rate of heat transfer required to maintain the inner surface at an igniting temperature. It was found by associated experiments that the premature ignition commonly obtained when hydrogen is used as the fuel for an Otto cycle engine is, in accordance with the experiments of this Part, due to an igniting temperature having been attained by the exhaust valve or the ceramic core of the spark plug. The engine experiments will be described in the next of the present series of papers.

INTRODUCTION

The combustion tube method used for experiments made to determine the effect of flow configuration on the oxidation and ignition of acetaldehyde and *n*-pentane in mixtures with air, described in Part XXIII (9), was again used for experiments with the hydrogen-air mixtures of this Part. It was shown by the experiments with acetaldehyde and pentane that ignition occurred at two temperature levels if the combustion tube was of silica but not if it was of steel.

When a chemically correct acetaldehyde-air mixture was supplied to the silica tube at 100 cc./min. the first igniting effect occurred when the maximum

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temperature of the wall, as measured on the outer surface, was 260°C. The second ignition occurred at a maximum wall temperature of 679°C. When a "correct" *pentane-air mixture* was supplied at the same rate, the first and second igniting temperatures were 321° and 571°C, respectively.

The first igniting effect was in both cases preceded and followed by cool flames which caused pressure fluctuations as they traversed the mixture. They disappeared before the occurrence of the second igniting effect. The temperature of the first ignition varied little with change of mixture strength or as rate of mixture supply was increased.

The temperature of the second igniting effect diminished rapidly as mixture strength was increased from weak to correct or as rate of mixture supply was increased from 100 cc./min. It was found also that the second igniting effect was not a consequence of the first. That is, the effects were not related and the characteristics of the second indicated that it occurred on the wall of the tube.

The first igniting effect, when obtained with the usual methods of experiment, is generally attributed to a chain reaction and mistakenly as preliminary to the second. The experiments mentioned above indicated however that the first ignition occurred when material nuclei were present in the reacting mixture. Thus it was evident that formaldehyde was formed by the partial oxidation of *n*-pentane or acetaldehyde on the wall of the tube at the temperatures of the first igniting effects. The formaldehyde was necessarily carried into the mixture ascending the tube by circulating convection currents. It is assumed that condensation products and the sudden decomposition of organic peroxide, if then formed, would provide the nuclei required for ignition. This hypothesis was supported by the results of engine experiments on the compression ignition of mixtures with air of acetaldehyde and of *n*-paraffins (7, 5, 8, 6).

Hydrogen cannot provide material nuclei of ignition in the manner described. The characteristics of its combustion and ignition in vertical combustion tubes and in engines are therefore of exceptional interest. The former are described in this Part; the latter are to be described in the next of the series.

A hydrogen-air mixture is always turbulent after admission to an engine cylinder. Combustion tube experiments with flow configuration dependent on turbulence as well as on heat convection are therefore described in this Part.

I. THE FLOW CONFIGURATION DUE TO HEAT CONVECTION IN VERTICAL COMBUSTION TUBES WITH TEMPERATURE GRADIENTS

Experimental Arrangements

The diagram of Fig. 1 was drawn with the horizontal scale double that of the vertical. It shows a combustion tube supported concentrically in a tubular electric furnace, and the ends of the annulus between the heated wall of the furnace and the tube closed by transite washers. The heated length of the furnace was $6\frac{1}{2}$ in. and the combustion tube projected three inches from its ends. The temperature gradients over the length within the furnace were determined by using a slidable wire ring of chromel and alumel with diametrically opposite junctions. A precision potentiometer was used to balance

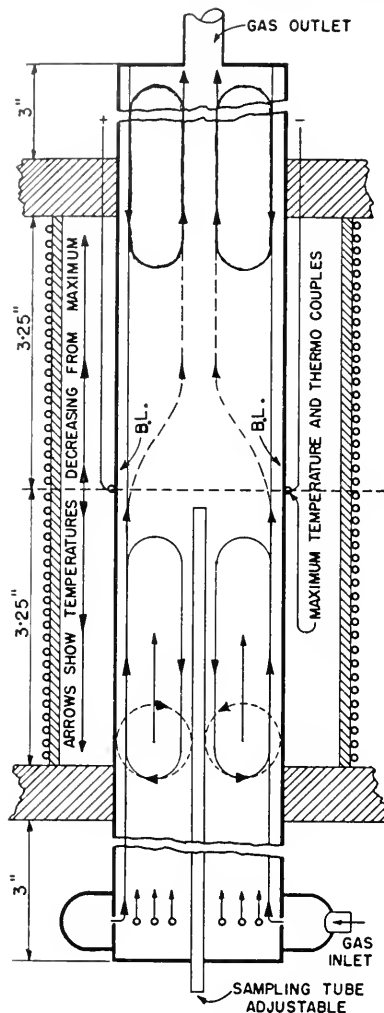


FIG. 1. Diagram showing the arrangement of a combustion tube concentrically in an electric furnace, the position of measurement of the apparent ignition temperature, the method of admitting gaseous mixtures, the convection circulations with non-turbulent gas flow, and the axis sampling device.

the thermoelectric potential against a standard cell. The equilibrium temperature gradients thus measured along a stainless steel tube, 28 mm. internal diameter and 1.58 mm. wall thickness, supported in a 2 in. diameter furnace are shown by the graphs of Fig. 2 for rates of heat input to the furnace varying from 135 to 344 watts; air or nitrogen was supplied at 200 cc./min. The graphs show that maximum wall temperature of the stainless steel tube was always attained at approximately the midsection of the tube length within the furnace. The position of maximum temperature was approximately half an inch above the midsection when the tube was of silica.

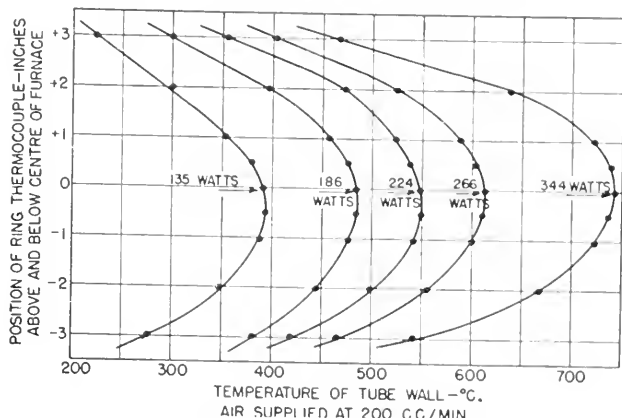


FIG. 2. Graphs showing surface temperature gradients from the midsection of the tube to the cool ends.

Hydrogen-air mixtures were admitted to the lower end of the combustion tube through a ring of holes in the periphery of a distributor type of inlet. When a mixture was supplied at rates commonly used for combustion experiments it tended to ascend along the heated wall of the tube and flow configuration depended on heat convection. The direction of flow through the distributor holes was however normal to the longitudinal axis of the tube and it was thus possible by increasing rate of mixture supply to create turbulence in the mixture passing through the tube while its space velocity was far less than would be required to exceed the critical Reynolds Number.

Flow Configuration Due to Heat Convection

An outline of the flow configuration in a transparent combustion tube when nitrogen was supplied through the distributor inlet at 100 cc. min. and the maximum wall temperature maintained at 500°C. was made visible by the method described in Part XXIII (9, p. 105). This outline, as shown by the solid flow lines of the diagram, Fig. 1, comprised a lower convection circulation extending over the rising temperature gradient below the midsection of the length of tube within the furnace and a shorter upper circulation over the falling temperature gradient above the midsection. The circulations are separated from actual contact with the tube wall by a boundary layer (B.L.) moving relatively slowly. The temperature of the mixture in the lower circulation is raised by heat from the wall, transmitted through the boundary layer. The mixture in the upper circulation, which passes over a falling temperature gradient, loses heat by transmission through the boundary layer to the wall before leaving the upper end of the tube. Thus its direction of motion was seen to be opposite to that of the lower circulation.

It was not possible to observe the pattern of flow within the convection circulations nor in the space between them. That within the lower circulation determines rate of heat transfer from the boundary layer to the mixture passing through the tube and the rate of reaction of the electrolytic gas in the

mixture as it ascends the tube. The ascending stream of this circulation receives initially all of the mixture supplied to the tube at rates which permit its existence. Its space velocity must therefore be higher than that of the descending stream in the constant pressure conditions of the experiments and also because temperature is raised continuously as it passes up the tube. It would be expected from considerations of gas dynamics that flow configuration within the circulation would comprise a procession of toroidal vortices moving upwardly with the mean space velocity of the mixture. A single vortex is shown in cross section by broken line circles, Fig. 1, and its upward movement indicated by arrows. The vortex is shown as penetrating the boundary layer. The thickness of the layer is shown to remain unchanged over the length of the combustion tube. The thickness would however diminish as penetration by the vortices increased. The degree of penetration would depend on the tendency of the diameter of the vortices to increase as the rotational velocity about their horizontal axis increased. This in turn would vary with the difference in temperature between the ascending and descending streams of the convection circulation.

II. TOROIDAL VORTICES AND RATES OF REACTION OF HYDROGEN-AIR MIXTURES ASCENDING A VERTICAL COMBUSTION TUBE OF STAINLESS STEEL

The procession of vortices ascending the rising temperature gradient of the lower convection circulation removes heated gas from the boundary layer and replaces it with cooler gas from the descending central stream. The rate of surface reaction as the hydrogen-air mixture passed up the tube could then be measured by the analysis of samples taken at points along the vertical axis. Experiments were carried out accordingly with the mixtures supplied to the stainless steel combustion tube at the relatively low rates required for the formation of convection circulations rather than general turbulence. The tube was 28 mm. internal diameter. The wall was 1/16 in. thick. The vertically adjustable sampling tube is shown by Fig. 1. It was of silica, 1/8 in. diameter and 1/16 in. bore. It is considered that samples remained unaltered while being drawn through the tube. Hydrogen was used in various concentrations in mixtures with air and corresponding concentrations of electrolytic gas, $2\text{H}_2 + \text{O}_2$, are given by the graphs of Fig. 3. Electrolytic hydrogen, as supplied

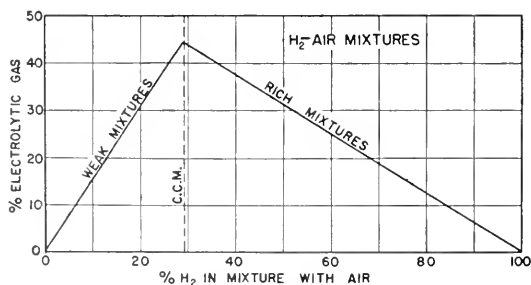


FIG. 3. Graph showing the relation between the concentration of hydrogen in a mixture with air and that of the electrolytic gas in the mixture.

by the Canadian Liquid Air Company, compressed to 2000 lb./sq. in. in steel cylinders, was used for the experiments. It was purified of oxygen before compression. It was then 99.95% hydrogen and nearly dry, the dew point being below minus 100°F. Experimental results are given by the graphs of Figs. 4, 5, and 6, and are described below in related paragraphs.

Fig. 4, Maximum Wall Temperature 550°C., Hydrogen Concentration 49%, Electrolytic Gas 32%, Mixture Supplied at 100 cc./min.

It is shown by Fig. 4 that reaction of the 32% of electrolytic gas in the mixture with air containing 49% of hydrogen began at approximately 3 in. below the midsection. That position is 0.25 in. within the furnace, and wall temperature would be 425°C. according to the relevant graph of Fig. 2. The

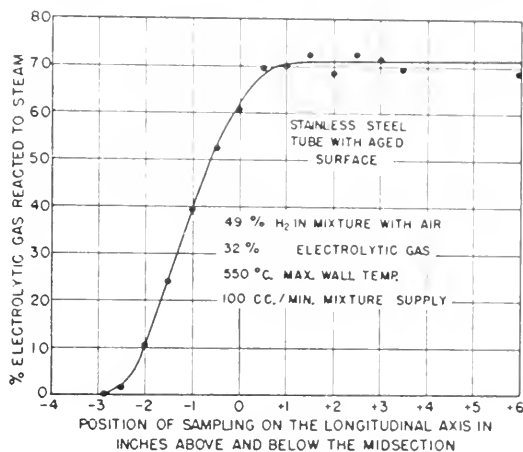


FIG. 4. Rate of reaction to steam on the surface of a stainless steel combustion tube. Maximum temperature 550°C., and 49% of hydrogen in mixture with air, supplied at 100 cc./min.

graph of the figure shows that rate of reaction increased slowly at first and then rapidly with the result that 60% of the concentration of electrolytic gas was reacted in the length of tube below midsection, over which wall temperature had increased from 425° to 550°C. Wall temperature then diminished and rate of reaction decreased to become zero at 1.5 in. above the midsection. Of the electrolytic gas in the mixture supplied to the tube, 71% had then been reacted to steam.

Fig. 5, Maximum Wall Temperature 755°C., Hydrogen Concentration 45%, Electrolytic Gas 34.6%, Mixture Supplied at 100 cc./min.

The temperature gradient below the midsection of the length of stainless steel combustion tube within the furnace was determined and is shown by graph B of the figure. Rates of surface reaction are given by graph A. It will be noted that the temperature of the tube wall was 605°C. at 3.0 in. below the midsection, that is 0.25 in. within the furnace, and that 30% of the electrolytic gas in the mixture had previously been reacted. The rate of reaction became so great that 80% of the electrolytic gas had been reacted at a position 2.6 in.

below the midsection. That is, a further 50% of the electrolytic gas was reacted while the boundary layer passed over 0.4 in. length of tube wall; the corresponding increase in wall temperature being from 615° to 715°C. over this length, see graph B. The increase in the reaction rate then diminished as the boundary layer passed over a length of 2.1 in. before reaction of the electrolytic gas was

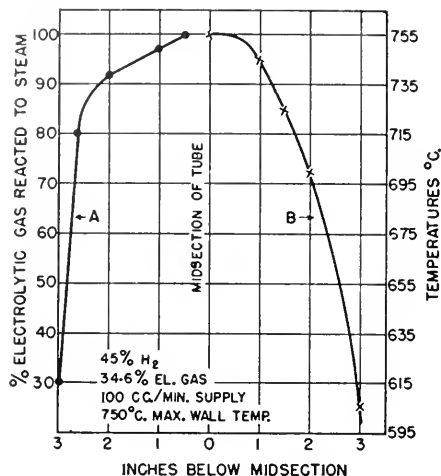


FIG. 5. Graph A. Rate of reaction to steam on the surface of a stainless steel combustion tube. Maximum temperature 750°C., 45% of hydrogen in mixture with air supplied at 100 cc./min.

Graph B. Temperature gradient on wall from midsection to 3 in. below that position.

100% complete at 0.5 in. below the midsection, which was at a temperature of 755°C. It will be seen by comparing graphs A and B that rate of reaction was generally similar to rate of increase of wall temperature.

Fig. 6, Maximum Wall Temperature 585°C., Differing Hydrogen Concentrations, Mixtures Supplied at 200 cc./min.

In addition to an experiment with a correct mixture, others were made with mixtures containing hydrogen in concentrations of 19 and 52%. These will be described as "weak" and "rich", and each contained 30% of electrolytic gas. Experimental results for rates of reaction are given by the graphs of Fig. 6.

The remarkable increase in rate of reaction that occurred on increasing the hydrogen concentration from 19 to 52% is shown by a comparison of Graphs A and B of the figure.

Reaction of the rich mixture began at 1.5 in. below the midsection of the tube and increased with such rapidity that 79% of the electrolytic gas had been reacted to steam at 2.0 in. above the midsection. There was no appreciable reaction between that position and the tube outlet. Reaction of the weak mixture began at a position one half inch closer to the midsection and 25% only of the electrolytic gas had been reacted at 2.0 in. above the position. There was no further reaction. The especially significant feature is that at the midsection of the tube where wall temperature had attained a maximum value

of $585^{\circ}\text{C}.$, 42% of the electrolytic gas in the rich mixture had been reacted and 11% only of that in the weak mixture. As each contained 30% of electrolytic gas when supplied to the tube, this means that at the position of maximum wall temperature where ignition is generally assumed to occur, the rich mixture contained 17.4% and the weak mixture 26.7% of electrolytic gas. Inflammability and the surface temperature required for ignition would vary accordingly.

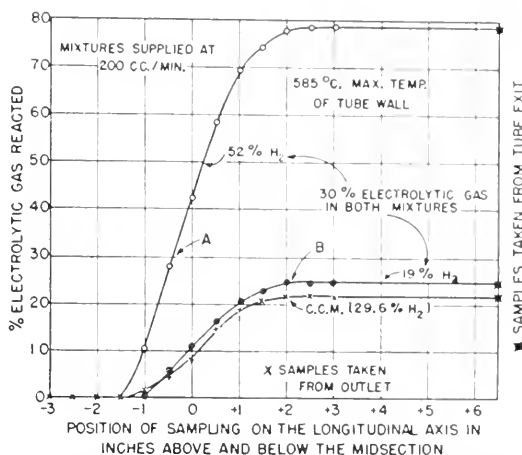


FIG. 6. Rates of reaction to steam on the surface of a stainless steel combustion tube. Maximum temperature $585^{\circ}\text{C}.$; 52, 19, and 29.6% of hydrogen in mixtures with air supplied at 200 cc./min.

A comparison of results for a chemically correct mixture with those for the mixture containing hydrogen in the concentration of 19% is of interest. The former contains hydrogen in the concentration of 29.6% and electrolytic gas in the concentration of 45%; the latter contains 30% of electrolytic gas. It is shown, however, by the relevant graphs of Fig. 6 that the rate of reaction of electrolytic gas was approximately 3% the greater for the mixture containing the smaller concentration of hydrogen.

III. THE IGNITION OF HYDROGEN-AIR MIXTURES SUPPLIED AT 100 CC./MIN. TO COMBUSTION TUBES OF VARIOUS MATERIALS

The combustion tubes were of stainless steel, silica, sillimanite, and carbon. The steel tube was $1\frac{1}{8}$ in. internal diameter and the others approximately 1.0 in. The wall of the carbon tube was $1\frac{1}{4}$ in. thick, that of the others $1\frac{1}{16}$ in. The tubes were arranged in a vertical electric furnace as shown by Fig. 1, with thermocouples set at the midsection of the length within the furnace in order to measure the maximum temperature attained by the wall. The object of the experiments was to determine the temperature at that position when ignition occurred. Thus an approximate temperature having been obtained, the tube was allowed to cool until the temperature fell from 30° to $40^{\circ}\text{C}.$ It was then reheated very slowly until ignition occurred again. Ignition temperatures thus

measured at the midsection of the tube must, according to the experiments of Section II, be higher than real values to an extent which varies with the degree of surface activity, with the concentration of hydrogen in excess of that required for a correct mixture, and with the time of contact of the mixture with the surface below the midsection, at a temperature such that reaction of electrolytic gas to steam can occur. The measured igniting temperatures will therefore be described as "*apparent ignition temperatures*" and the term abbreviated to A.I.T.

The Silica Tube

It is shown by Graph A, Fig. 7, that the A.I.T. was substantially constant with hydrogen concentration diminishing from 30 to 20%. Then as the concentration was further reduced to 8% and the concentration of excess oxygen increased accordingly, the increase in A.I.T. was 3°C. only. When however hydrogen concentration was *increased* from 30 to 80%, the A.I.T. rose slowly

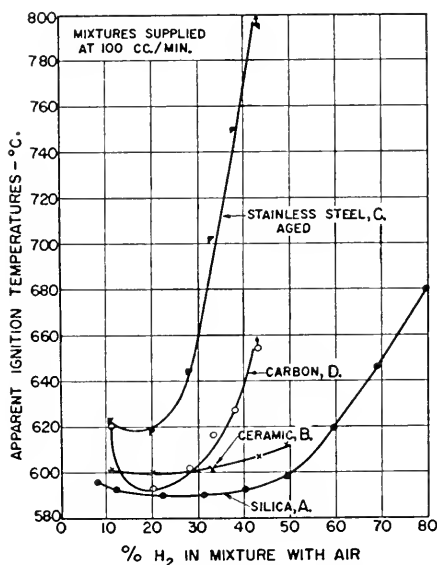


FIG. 7. Apparent ignition temperatures, combustion tubes of various materials, hydrogen concentration increasing from 10% in mixtures with air supplied at 100 cc./min.

at first and then rapidly to a value of 680°C. The concentration of electrolytic gas was approximately 12½% in mixtures containing either 8 or 80% of hydrogen, but the values for A.I.T. were 595° and 680°C. respectively. This result, obtained with a low rate of mixture supply and what is reputed to be a stable surface of minimum activity, illustrated the rise in A.I.T. due to the increase in rate of reaction below the midsection of the tube that is obtained as hydrogen concentration is increased.

The Sillimanite (Ceramic) Tube

The material was reputed to be a mixture of 62% alumina, 35% silica, and

3% oxides of other metals. The tube was used for the purpose of demonstrating the effect of spark plug cores of similar material in igniting hydrogen air mixtures in an engine. Values for A.I.T. were determined accordingly for mixtures with air containing hydrogen in concentrations ranging from 10 to 50%. This is equivalent to mixtures ranging from 75% weak to 140% rich, as used in an engine. Graphs A and B show that values obtained for A.I.T. varied in the same manner for sillimanite and silica but that those for sillimanite were approximately 10°C. the higher.

The Stainless Steel Tube, Aged Surface

The tube had been used for experiments described in Section II. The surface had become oxidized and is therefore described as "aged". It will be seen by Graph C of Fig. 7 that a minimum of 620°C. was observed for the A.I.T. when the mixture with air contained hydrogen in the concentration of 20% and that a slight rise in A.I.T. occurred on reducing the concentration to 10%. However on increasing the hydrogen concentration, values for A.I.T. increased so rapidly that with 42% of hydrogen in the mixture, ignition was not obtained until the midsection was heated to 828°C.; not shown, Fig. 7. This ignition must therefore have occurred in the tube below the midsection of maximum temperature. This result is as would be expected from the experimental results shown by Fig. 5. These were obtained with the same combustion tube and the same rate of mixture supply, and all of the electrolytic gas in a mixture containing 45% of hydrogen was reacted to steam below a midsection temperature of 755°C.

The Carbon Tube

It will be seen by reference to Graph D of Fig. 7 that a minimum value of 592°C. was obtained for the midsection temperature required for the ignition of a hydrogen-air mixture in the carbon tube. The mixture then contained hydrogen in the concentration of 20% and the ignition temperature was approximately that obtained with the silica tube and the same concentration of hydrogen. Carbon tube ignition temperatures unlike those obtained for the silica tube rose rapidly as the concentration of hydrogen was either increased or diminished and ignition temperatures of 620° and 627°C. were obtained with hydrogen concentration of 10 and 38% respectively. On increasing the hydrogen concentration to 42% a temperature higher than 654°C. was required for ignition. The carbon surface was then glowing brightly and values for ignition temperatures were not obtainable.

It was found however that the carbon and graphite tubes used for the experiments were in some degree transparent to hydrogen. It is probable therefore that the rise in A.I.T. that occurred on increasing hydrogen concentration was affected accordingly.

The experimental results are however of significance, because it was shown by those given in Part XXIII (9, p. 108) that mixtures of air with pentane or acetaldehyde were not ignited in the carbon tube or in a graphite tube although the midsection temperature was raised to 760°C.

IV. IGNITION TEMPERATURES AS AFFECTED BY SURFACE STATE AND COMBUSTION TUBE MATERIAL, FLOW CONFIGURATION BEING DEPENDENT ON HEAT CONVECTION

Difficulties have been encountered in the obtaining of repeatable values for A.I.T. of hydrogen-air mixtures, especially when the steel combustion tubes are used, and rates of supply are such that flow configuration is governed by heat convection. The difficulties are due to changes in surface state that occur in the course of a series of experiments for which hydrogen concentration is varied. The extent to which observed values are not repeatable increases as hydrogen concentration increases.

Numerous methods of surface treatment were tried in attempts to obtain repeatable values for A.I.T. The methods, in addition to those commonly applied to vitreous surfaces, included the reduction of surface oxide by long exposure to hydrogen while the midsection of the tube was maintained at 680°C. as well as the formation of surface oxide by a similar treatment with oxygen. Nearly repeatable, but relatively low values for A.I.T. were obtained if, before beginning experiments with a stainless steel tube, the surface were cleaned by the usual method of pickling with a hot 10% solution of hydrochloric acid in water. Nearly repeatable but relatively high values for A.I.T. were obtained if the stainless steel surface were aged by continuous use after a coating of oxide had been formed. The "activity" of the surface thus formed was responsible for the relatively high values for A.I.T. obtained when hydrogen was in excess of the concentration required for a correct mixture with air. The activity of the surface diminished during a period of disuse and a period of reuse was required to regain repeatable values for A.I.T.

Values for A.I.T., Aged and Clean Stainless Steel Tubes

Mixtures containing hydrogen in concentrations rising from 10% were supplied to the tubes at rates of 200 cc./min. Experimental results are given by Fig. 8.

Graph A of the figure shows the values obtained for A.I.T. when the mixtures were supplied to the aged stainless steel tube. This tube had been used for the experiments described in Sections II and III.

Graph B shows the results obtained when a similar stainless steel tube was used after the surface had been cleaned by the pickling method. The experimental results for the similar tubes with different varieties of surfaces show differences in values of A.I.T. increasing to a remarkable extent as hydrogen concentration in the mixture supply was increased. Thus when a correct mixture was supplied, the values for A.I.T. were 640° and 610°C. for the aged and clean tubes respectively. When the hydrogen concentration was 40% the respective values for A.I.T. were 745° and 615°C. and 790° and 635°C. when hydrogen concentration was 50%. Values for A.I.T. were not obtainable below 800°C. when the mixture supplied to the aged tube contained hydrogen in greater concentration than 52% but were obtained for concentrations increasing to 80% in mixtures supplied to the clean tube.

Values for A.I.T. lying between those shown by the graphs of Fig. 8 were

obtained after various other methods of treatment had been used but were not repeatable. Pretreatment of the aged surface with hydrogen led to higher values being obtained for A.I.T. when oxygen was in excess in the mixtures supplied, but the values were not repeatable.

Graph A of Fig. 8 may be taken to represent the upper limit of repeatable values for A.I.T. and Graph B, the lower.

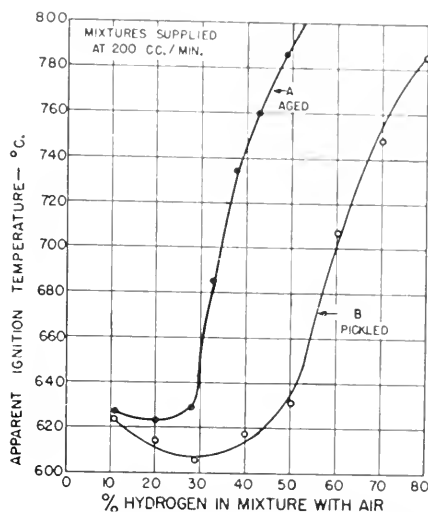


FIG. 8. Apparent ignition temperature as affected by the surface state of a stainless steel combustion tube. Hydrogen concentration increasing from 10% in mixtures with air, supplied at 200 cc./min.

Values for A.I.T. Mild and Stainless Steel and Silica Tubes

The mild steel tube was cleaned by pickling before being used. The silica surface was not treated in any way. The hydrogen-air mixtures were supplied at 200 cc./min. and an additional experiment with the silica tube was carried out with mixtures supplied at 100 cc./min. The experimental results are shown by Graphs A, C, and D of Fig. 9. Graph B for the clean stainless steel tube is reproduced from Fig. 8.

The surface of the mild steel tube oxidized rapidly and tended to pit and scale. It will be seen, Graph A, that a minimum of 650°C. was obtained for the A.I.T. with a hydrogen concentration of 20%. The values then increased so rapidly as the concentration of hydrogen was increased or diminished that A.I.T. values less than 800°C. were not obtained with a hydrogen concentration greater than 33%, or less than 700°C. when the concentration was less than 10%. Graph C, obtained for the silica tube with mixtures supplied at 100 cc./min., follows the pattern of Graph B for the stainless steel tube and the A.I.T. for a correct mixture was lower by 10° only. Moreover the values for A.I.T. varied little for hydrogen concentrations ranging from 10 to 10%. An especially significant result is the relatively rapid rise in A.I.T. obtained as

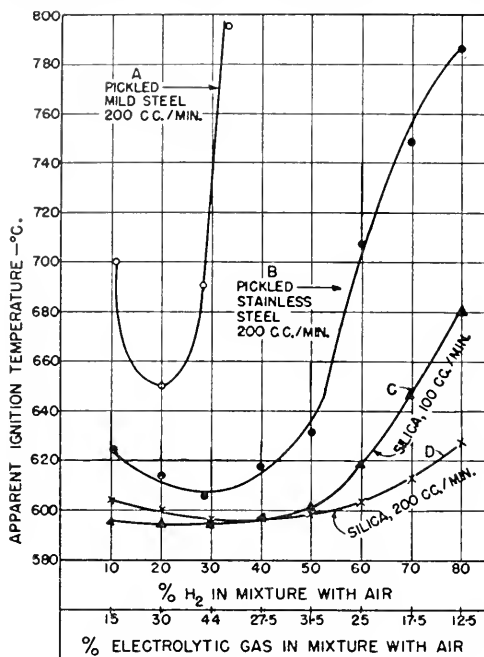


Fig. 9. Apparent ignition temperatures, hydrogen increasing in concentrations from 10% in mixtures with air supplied to combustion tubes of mild steel, stainless steel, and silica at 200 cc./min. and to the silica tube at 100 cc./min.

hydrogen concentration was increased from 40 to 80% in the mixture supplied at 100 cc./min. as compared with that obtained over the same range of hydrogen concentration when the mixtures were supplied at 200 cc./min. as shown by Graph D.

V. APPARENT IGNITION TEMPERATURES AS AFFECTED BY REPLACING CONVECTION CURRENTS WITH TURBULENCE

The design of the distributor inlet used for admitting hydrogen-air mixtures to the lower ends of vertical combustion tubes was described in Section I and illustrated by Fig. 1. It is such that turbulence tends to be created in the mixture as admitted, on increasing the rate of supply. A "stilling" length of tube was not provided and initial turbulence would persist as the gaseous mixture passed upwardly through combustion tubes of the length and diameter used for the experiments of this Part. Thus, turbulence, after being initiated by increasing rate of mixture supply to the requisite value, would increase as rate continued to be increased although the Reynolds Number, even at the highest rate used for experiments, was far below the critical value. The effect on flow configuration would be that circulating convection currents would tend to be replaced by turbulence when rate of mixture supply exceeded a value which can be determined by experiment only. Experiments carried out accordingly are described in this Section.

Stainless Steel Tube with Clean Surface

The changes in the relation between A.I.T. and hydrogen concentration that occurred as the mixture supply was increased from 60 to 2000 cc./min. are shown by the family of graphs, Fig. 10. It will be seen that they fall into two groups of plainly different characteristics.

The first group comprises the graphs for values of A.I.T. obtained when mixtures were supplied at 60 to 400 cc./min. Definite minimum values for A.I.T. differing little from 608°C. were then obtained when the mixture was approximately correct. Values of A.I.T. increased rapidly with increasing concentrations of hydrogen. The rate of increase diminished as rate of supply was increased to 400 cc./min. Thus for example when the concentration of hydrogen in the mixture was 50%, the A.I.T. was 755°C. with a rate of supply of 60 cc./min. and 630°C. with a rate of 400 cc./min. It is indicated by the experimental results and those described earlier in this Part that circulating convection currents persisted in the mixture passing through the tube until rate of supply was increased to at least 400 cc./min.

The second group comprises the graphs for values of A.I.T. observed when mixtures were supplied at rates of from 700 to 2000 cc./min. It will be seen that the increase in rate of supply of from 400 to 700 cc./min. was accompanied by an increase in the minimum value of A.I.T. from 608° to 622°C. Moreover, the higher value instead of increasing with an increase in hydrogen concentration, remained substantially constant over the hydrogen concentration range of 30 to 50%. The minimum value for A.I.T. continued to increase with increases in the rate of mixture supply and as this occurred it extended over an increasing range of hydrogen concentration. Finally when rate of supply had been increased to 2000 cc./min., a minimum value for A.I.T. of $650 \pm 2^\circ\text{C}$. was obtained for hydrogen concentrations ranging from 30 to 80%.

As the concentration of hydrogen was decreased from 30 to 10%, values of A.I.T. increased at nearly similar rates as the rate of mixture supply was increased from 700 to 2000 cc./min. The total increase was 15°C. with mixtures supplied at 700 or 1000 cc./min. and 20°C. at a rate of 1500 or 2000 cc./min.

The radical change in ignition characteristics that occurred on increasing rate of mixture supply from 400 to 700 cc./min. is attributed to circulating convection currents having been displaced by turbulence.

Experiments with Correct Hydrogen-Air Mixtures Supplied at 50 to 2500 cc./Min. to Silica and Clean Stainless Steel Tubes

The values obtained for apparent ignition temperatures as rate of supply of a correct mixture was increased from 50 to 2500 cc./min. are given by the graphs of Fig. 11. It is shown by Graph B of the figure that when the combustion tube was of clean stainless steel, the relation between A.I.T. and rate of mixture supply follows closely that obtained in the earlier experiments with a similar tube as shown by the graphs of Fig. 10.

Experiments were not carried out earlier with a silica tube and rates of mixture supply greater than 200 cc./min. The A.I.T. at this rate as shown by

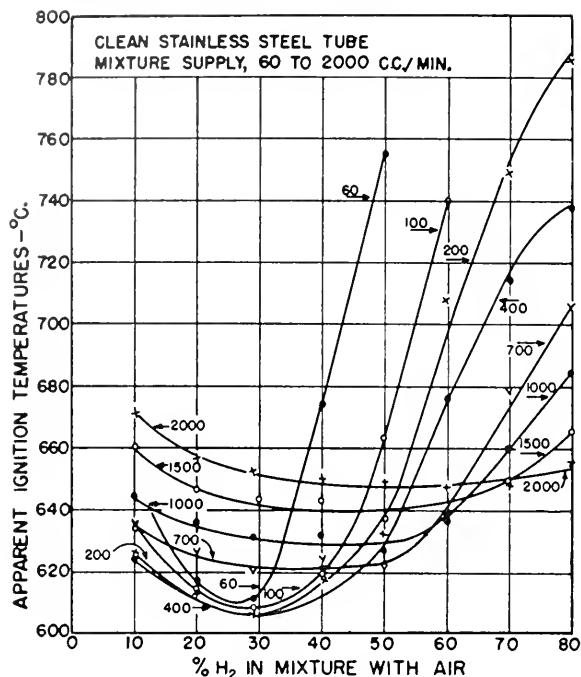


FIG. 10. The change in the characteristics of apparent ignition temperature obtained when, by increasing rate of mixture supply, the flow configuration due to heat convection is replaced by turbulence. Hydrogen concentrations ranging from 10 to 80% in mixtures with air supplied to a stainless steel combustion tube at 50 to 2000 cc./min.

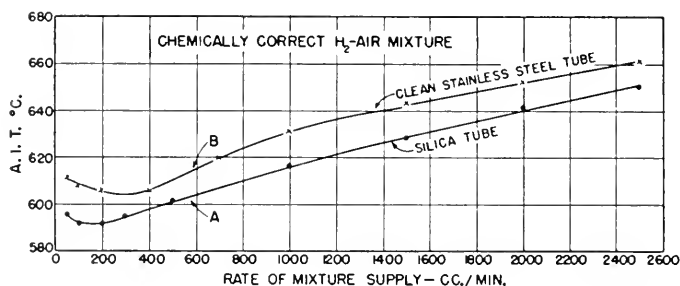


FIG. 11. The effects on apparent ignition temperatures obtained on replacing flow configuration due to heat convection by that due to turbulence, correct hydrogen-air mixtures supplied to silica and stainless steel combustion tubes at 50 to 2500 cc./min.

Graph A of Fig. 11 was 590°C. It was 604°C. with the clean stainless steel tube, Graph B of the figure. The respective values obtained earlier, as shown by Fig. 9, were 596° and 607°C. The consistency is as good as would be expected in view of small changes in surface state which cannot be avoided. The significant feature of the experiments is that when a *correct* mixture was supplied to the combustion tubes, the difference between values obtained for A.I.T. varied little as circulating convection currents were replaced by turbulence.

Experiments with Mixtures Containing 50% of Hydrogen Supplied at 50 to 2500 cc./Min. to Silica and to Stainless Steel Tubes, Clean, and Aged

It was shown by the experimental results, Fig. 10, obtained when a clean stainless steel tube was used, that circulating convection currents tended to be replaced by turbulence as the rate of mixture supply exceeded 100 cc./min. and that the transition had been completed when the rate was 700 cc./min. These results, obtained with one variety of surface, do not illustrate the corresponding effect on rate of reaction, and the consequent value of A.I.T., of other more or less active surfaces when hydrogen concentration is greater than required for a correct mixture. Surfaces in order of increasing activity are provided by combustion tubes of silica, stainless steel with a clean and with an aged surface. Values obtained for A.I.T. when using these tubes and a mixture with air containing 50% of hydrogen are given by the graphs of Fig. 12. They show that when flow configuration was due to heat convection, the

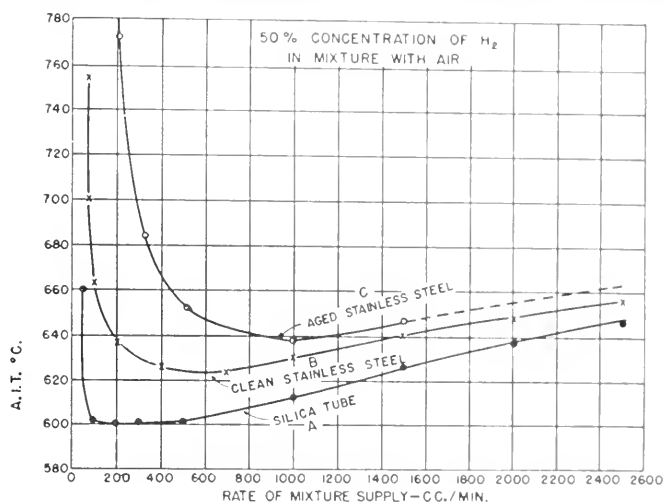


FIG. 12. The effects on apparent ignition temperature obtained on replacing flow configuration due to heat convection by that due to turbulence, 50% of hydrogen in mixtures with air supplied at 50 to 2500 cc./min. to a silica tube and to a stainless steel tube with a clean and with an aged surface.

values of A.I.T. and the extreme difference between them, which was dependent on the degree of surface activity, decreased rapidly as mixture supply was increased and time of residence diminished, and that after turbulence had been established, the values *increased* slowly and differences due to the degree of surface activity tended to disappear. Thus values of A.I.T. began to rise at rates of mixture supply of 400, 600, and 1000 cc./min. when the tubes used were of silica, and of stainless steel with a clean and with an aged surface, respectively. The over-all difference in the values of A.I.T. of nearly 180°C., which was obtained with a mixture supply of 200 cc./min., diminished to 37°C. on increasing the rate to 700 cc./min. and to 18°C. as it was further increased to 2500 cc./min. Thus surface activity, which was a predominant factor in

respect of the values obtained for A.I.T. when mixtures containing excess hydrogen were supplied at relatively low rates, became of very secondary importance when convection circulations were replaced by turbulence.

Apparent Ignition Temperatures were, as explained earlier, measured by thermocouples on the outer surface of a combustion tube at the position of maximum temperature. The effective temperature is that on the inner surface at the same position. This temperature has been found to be the lower by 10° or 12°C. , at small rates of mixture supply. The difference would be expected to increase as rate of supply of turbulent mixture increased. This effect and the drop in temperature of the gas passing through a combustion tube when the area of heated surface remains nearly constant while the velocity of the gas flow increases may account for the rise in values of A.I.T. that occurred after turbulence became established.

VI. PEROXIDES

Numerous attempts were made to detect hydrogen peroxide by titration of an aliquot of the liquid reaction product as trapped in condensers cooled with a dry ice - acetone mixture. Peroxide was not detected in the product from either the silica or the steel combustion tube when a 0.02 *N* potassium permanganate solution in water was used for the titration. It may be concluded that peroxide was not formed when reaction occurred in the flow configuration conditions of the experiments or, if formed, decomposition must have occurred before the mixture left the combustion tube.

DISCUSSION

Many attempts have been made to show that mixtures of hydrogen with air or oxygen can be ignited apart from surfaces, by the application of heat. A comprehensive description of the methods tried and the results obtained is given by Jost (4, pp. 3-46). It appears accordingly that flow configuration has not been regarded as a determining factor in respect of the temperatures required for ignition. Dixon (2), for example, when using his concentric tube method, sought to avoid the wall effect by increasing the diameter of the outer tube which was heated electrically. He does not seem to have realized that by injecting the hydrogen through a small orifice in the end of the inner tube which projected halfway up the length of the outer one, a contra flow was set up which would bring reacting mixture into contact with its surface. It appears therefore that ignition occurred when the surface of the inner tube attained the necessary temperature and that the observed delay periods represented merely the times required.

Alyea and Haber (1) used the crossed streams method of determining the ignition temperature of mixtures of hydrogen and oxygen. The tubes carrying the heated gases to orifices in their ends were apparently far enough apart to prevent recirculation around them of a mixture of the gases. In these conditions no ignition occurred at reduced pressures of from 10 to 200 mm. Hg at temperatures up to 540°C. if pressure were gradually reduced so that what is generally regarded as the normal explosion region was entered. When however a surface

of quartz, porcelain, or glass was placed at the junction of the crossing streams, an ignition always occurred when the explosion region was approached or entered.

Goldmann (3) using normal pressure and higher temperatures found that ignition occurred when one or other of the streams of hydrogen and oxygen was heated to 560°C . or higher. It was concluded that formation of active atoms or radicals producing a chain reaction leading to ignition was possible in the gas phase at temperatures above 560°C . but that at lower temperatures and pressures a surface was necessary for their production. The streams of gases issued from orifice tubes only a few millimeters apart and, in the light of the flow configuration experiments described in this Part, it is probable that a mixture of the reacting gases circulated about the tube carrying the heated gas. Thus it is possible that ignition as observed by Goldmann was a surface effect instead of one occurring in the gas phase.

Flow Configuration Due to Heat Convection in a Vertical Combustion Tube

The mixture supplied to the lower end of the tube forms a convection circulation over the lower temperature gradient and is separated from the wall by the boundary layer. When however reaction occurs on the surface the reacted mixture containing steam diffuses through the boundary layer to join the ascending stream of the convection circulation and is replaced by less reacted mixture diffusing through the boundary layer in the opposite direction. The normally laminar flow in the boundary layer is disturbed accordingly. The rate of surface reaction at a particular position on the tube surface will be governed in the circumstances by its temperature, the nature of the surface, and the rates of diffusion which would in turn depend on the thickness of the boundary layer, its density, and the density of the mixtures diffusing through it. The densities would diminish on increasing the concentration of hydrogen in the mixture with air. The concentration of steam in the mixture at the position of maximum temperature would then depend on the factors mentioned and rate of supply of unreacted mixture to the tube.

If the oppositely moving streams of the lower circulation form toroidal vortices instead of remaining intact, all of the effects mentioned would increase in magnitude; rates of diffusion especially would increase because of the tendency of the vortices to expand and thereby reduce the thickness of the boundary layer. Its thickness has been shown by Fig. 1 as uniform but in reality it would increase or diminish as the vortices contracted or expanded according to temperature difference between the oppositely moving streams of the convection circulation.

The consequent effect of the factors described above on rates of reaction is shown by experiments described in Section II. For example, when a mixture containing hydrogen in a concentration of 15% was supplied to a stainless steel tube with an aged surface at 100 cc. min. while the midsection was maintained at 775°C ., all of the electrolytic gas in it was reacted to steam in the length of tube below the midsection. The effect of excess hydrogen is again illustrated by a comparison of the rates of reaction obtained when mixtures

containing 19 and 52% of hydrogen were supplied to the tube at 200 cc./min. while the midsection temperature was maintained at 585°C. Both mixtures contained 30% of electrolytic gas but, as shown by the graphs of Fig. 6, 11% was reacted when the mixture contained excess oxygen and 42% when the mixture contained excess hydrogen. Conditions were similar in both cases except that, as supplied to the tube, the density of the mixture containing excess oxygen was 60% the greater. Secondary effects which are difficult to evaluate were the more rapid formation of steam in the mixture containing excess hydrogen and the smaller effect of the vortices in the less dense mixture to penetrate the boundary layer.

The relative rates of reaction in further experiments were taken to be indicated by the corresponding values of the A.I.T. It is of interest accordingly that when correct mixtures were used, the A.I.T. observed with a clean stainless steel tube to which the mixture was supplied at 200 cc./min. was approximately 10°C. only higher than when a similar mixture was supplied to a silica tube at either 100 or 200 cc./min., Fig. 9. The A.I.T. observed when the silica tube was used, if it had been measured on the inner wall, would differ little from the value of 585°C. assumed by Dixon to have been obtained apart from a surface (2). The rise in the values of A.I.T. as the concentration of hydrogen in mixtures supplied to the silica tube was increased is attributed to the decreasing density of the boundary layer and it will be noted that the rate of rise of A.I.T. increased on reducing the rate of mixture supply from 200 to 100 cc./min. as might be expected accordingly.

Turbulence in the Combustion Tube and in the Combustion Chamber of an Engine

The establishment of turbulence in the combustion tube was accompanied by a decrease in the thickness of the boundary layer and in the time of residence of the hydrogen-air mixture in the tube. There was therefore an increase in the rate of abstraction of heat from the inner surface of the tube and it became necessary to compensate for this effect by raising the temperature on the outer surface. Then because of the decrease in time of residence there was a diminution in the surface reaction of electrolytic gas to steam in the length of tube below the midsection; the variation in the amount of reaction due to differences in the nature of the tube surface also diminished. There was in consequence an increase in temperature required for ignition, as measured on the outer wall at the midsection, and a decrease in the effect of changes in the nature of the surface, on that temperature. There was then a corresponding decrease in the rise of the apparent ignition temperature that was observed in earlier experiments carried out at relatively low rates of supply of mixtures containing hydrogen in excess of the concentration required for a correct mixture. The combined effect of the factors mentioned increased as turbulence was increased on increasing rate of mixture supply, and thereby decreasing the time of residence in the tube. The result was that with a mixture supply of 2000 cc./min., the surface temperature required for ignition remained substantially constant while hydrogen concentration was increased from 30 to 80% and varied little with changes in the nature of the surface. The total difference due to changing

from a silica to an aged stainless steel surface was approximately 20°C . It was more than 200°C . when a mixture containing 50% of hydrogen was supplied at 200 cc./min. and flow configuration depended on heat convection.

Experiments with hydrogen-air mixtures supplied to an Otto cycle engine were carried on in association with the combustion tube experiments. Turbulence in both cases was increased by increasing the rate of mixture supply. This tended to reduce the temperature of the wall of the combustion tube but to *raise* the temperature of the wall of the combustion chamber of the engine, if it was operated at full throttle. The increase occurred because the increase in rate of mixture supply to the engine was obtained by increasing speed and consequently the heat load. The indirectly cooled surfaces of the exhaust valve and the ceramic core of the spark plug then tended to attain an igniting temperature in respect of the mixture as speed was raised in an attempt to develop maximum horsepower. The occurrence of premature ignition, in the circumstances, was avoided by a reduction in the exposed area of the ceramic core of the spark plug and by a reduction of the temperature of the exhaust valve, mainly by sodium cooling. The experiments will be described in the next of the present series of papers.

ACKNOWLEDGMENTS

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THE OXIDATION, DECOMPOSITION, IGNITION, AND DETONATION OF FUEL VAPORS AND GASES

XXVII. THE HYDROGEN ENGINE¹

BY R. O. KING² AND MOGENS RAND³

ABSTRACT

Experiments made with hydrogen as the fuel for an Otto cycle engine show that optimum performance in terms of power and economy is limited only by preignition arising from the temperatures attained by the ceramic core of the spark plug or by the exhaust valve, or from nuclei formed by pyrolysis of lubricating oil vapor. On reduction of the magnitude of these igniting effects it became possible to operate the engine with speeds rising to 1800 r.p.m. and the compression ratio fixed at 12:1. A value of 116 p.s.i. for I.M.E.P. with an indicated thermal efficiency of 37% was obtained when the maximum power mixture strength was used. A value of 90 p.s.i. was obtained for I.M.E.P. with an indicated thermal efficiency of 47% with a mixture 55% weak. These values exceed, by a wide margin, any recorded in the literature of the subject.

INTRODUCTION

Results in conformity with the nuclear theory of ignition, as stated in Part IV (7), were obtained when hydrogen was used as the fuel for experiments with a C.F.R. knock rating engine (Part V (12)). These experiments were carried out at the standard knock rating speed of 900 r.p.m. and with compression ratios rising to 10:1. Ignition otherwise than by the electric spark did not occur unless finely divided carbon had been allowed to accumulate in the combustion chamber. It was found later that the carbon was a product of the pyrolysis of lubricating oil vapor. A similar igniting effect occurred when charcoal dust was added to the hydrogen-air mixture before it entered the combustion chamber and when in subsequent experiments the laboratory atmosphere was impregnated to an unusual degree with concrete dust (11). This was of especial interest in that the nuclei were not combustible. A significant feature of the experiments was the occurrence of some degree of preignition on increase of the temperature of the jacket coolant from 110° to 212°F. This effect according to the nuclear theory of ignition would be due to a surface in the combustion chamber having attained an igniting temperature or to nuclear ignition arising from an increase in the rate of vaporization of lubricating oil. The surfaces that would be expected to attain an igniting temperature were those of the exhaust valve, and the ceramic core of the spark plug or of its central electrode. The most effective way of raising the temperature of these indirectly cooled surfaces would have been to increase the heat load by increasing engine speed but the unbalanced C.F.R. knock rating engine

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was not suitable for operation at speeds higher than 900 r.p.m. The engine experiments were therefore discontinued until a C.F.R.-F4 engine, balanced for high speed operation, became available for the new series of experiments described in this Part.

Experiments with combustion tubes of materials similar to those in the combustion chamber of the engine were however initiated in order to determine the wall temperature required for the ignition of hydrogen-air mixtures passing through them and are described in Part XXVI (10).

EXPERIMENTAL ARRANGEMENTS AND METHODS, PRESENTATION OF RESULTS

The Engine

The C.F.R.-F4 engine, bore $3\frac{1}{4}$ in. stroke $4\frac{1}{2}$ in., is fitted with balancing pistons in the crank case, as required for high speed running. The cast iron piston is fitted with an oil scraper ring and three pressure rings. The engine was direct connected to a d-c. generator arranged as a swinging field dynamometer for the measurement of B.H.P. directly and of I.H.P. by the motoring method. Provision was made for the measurement of compression ratios varying from 4 to 20:1.

Camshafts which provided suitable valve timing for speed ranges of 900 to 1200 r.p.m. and 1200 to 1500 r.p.m. were available. They will be described respectively as low and high speed camshafts. The valve timing and lift are given in the appendix to this Part.

Cylinders with holes for three spark plugs in the wall and one in the head were available. One was fitted with a sodium cooled exhaust valve, and others with the C.F.R. standard uncooled valve of silchrome steel. The types of the cooled and uncooled valves are illustrated by Fig. 15 of the appendix. A plain or a shrouded inlet valve could be used in either cylinder.

Exhaust Valve Surface State

The surface state of the face of the exhaust valve varies with time of use and this was found to have an appreciable effect on the temperature required for the ignition of other than weak hydrogen-air mixtures. Exhaust valves with two varieties of surface state were used, namely *clean* and *aged*.

A valve cleaned with abrasive material and then washed with alcohol before a set of experiments was begun is described as *clean* although it ceases to remain in that condition to an extent depending on the time required to complete a set. A running time of from three to four hours is generally required.

An *aged* valve is one that has been used for many sets of experiments and cleaned only by washing with alcohol, before a set of experiments is begun.

The Ignition System

The designs of spark plugs used for the experiments are illustrated by Fig. 14 of the appendix. Champion C.F.R.-8 was until recently the standard spark plug for use with the A.S.T.M.-C.F.R. method of knock rating. It is a "hot" variety, near the top of the commercial heat scale. Spark plugs K.L.G. 100 and Champion R 2-S were used as cool varieties.

The coil ignition supplied as standard had been found to be ineffective with hydrogen-air mixtures at a C.R. of 10.0, unless the spark gap were reduced to 0.012 in. A special Auto-Lite ignition system was used for experiments made subsequently with hydrogen and other gases and it was then possible to increase the spark gap to 0.025 in. if necessary. The system is described in the appendix to Part XIII (9).

Temperature Control

It was found in the course of preliminary experiments that as the heat load carried by the engine was raised, by increasing speed for example, it became necessary to control the temperatures of the air and hydrogen supplied to the engine if repeatable results were to be obtained. The temperature of the air drawn from the laboratory atmosphere was subject to variations of approximately 40°F. The method used for maintaining the supply of air and hydrogen at a nearly constant temperature of 65°F. is described in the appendix to this Part.

Water was used as the jacket coolant and temperatures lower than 212°F. were controlled automatically by the thermostatic method described in Part XIII (9, pp. 152-153). The flow of water through the cylinder jacket could be controlled by this method to ensure that the temperature at the outlet was never more than 5°F. higher than that at the inlet.

The lubricating oil in the crank case sump was maintained at 110°F. by an exterior electric heater with manual control. Oil pressures maintained at speeds of 900, 1200, 1500, and 1800 r.p.m. were 18, 21, 23, and 25 p.s.i. respectively.

The Hydrogen Supply

Electrolytic hydrogen as supplied by the Canadian Liquid Air Company, Toronto, compressed to 2000 p.s.i. in steel cylinders was used for the experiments. The hydrogen was reputed to be 99.95% pure and as compressed was nearly dry, the dew point being below minus 100°F. The lower calorific value as used for calculations of thermal efficiency was taken as 274.5 B.T.U. per cu. ft., at 60°F. and 30 in. Hg. The method used for the measurement of the rate of hydrogen supply to the engine is described in the appendix to this Part.

The Lubricating Oil

A separate series of experiments with lubricating oils indicated that the least amount of residue remained in the combustion chamber after Ucon had been used. This is a synthetic lubricant made by the Carbide and Chemicals Corporation with a base composed of polyalkylene glycols and derivatives. The grade selected for the experiments is described as L.G. 300 X, which indicates that it is water insoluble, has a viscosity of 300 Saybolt universal seconds, and is oxidation inhibited but without additives. According to A.S.T.M. tests, the viscosity index is 142, ash less than 0.01%, carbon residue also less than 0.01%, and water less than 0.25%. The viscosity is close to S.A.E. 30 at 210°F. and the same as S.A.E. 20 at 130°F.

Methods of Experiment

The engine was always prepared for a particular set of experiments by being dismantled for a top overhaul. The cylinder, piston, and rings were then washed with acetone and alcohol. The valves were inspected and hand lapped into their seats if signs of leakage were detected. On conclusion of the set it was verified, by measurement of compression pressure before the engine had cooled, that piston sealing had not deteriorated.

The lubricating oil and the jacket cooling water were heated electrically to working temperatures before a set of experiments was begun. The engine was then started on a hydrogen-air mixture 50% weak and run for at least 30 min. The mixture was then reduced to the leanest on which the speed selected for the first experiment could be maintained. This was always the lowest of the speeds to be used for a set of experiments. The engine was then run for 15 min. before a determination of the optimum spark timing.

Hydrogen burns with high velocity in mixtures with air approaching and exceeding the correct value and relatively slowly when in small concentration in air, and the ignition timing required for maximum power output when a particular mixture strength and engine speed was used can be determined with accuracy, solely by a series of lower measurements. Brake horsepower was measured accordingly for a series of ignition timings giving rising and falling values for power output and the optimum timing was then obtained from a plot of results, as described in Part XII (8, pp. 438-439).

Presentation of Experimental Results

Experiments were carried out at engine speeds rising to 1800 r.p.m. and with compression ratios of 10 and 12:1. Comprehensive performance data are given by graphs plotted on a mixture strength base as used for experiments with liquid fuels. A "correct" mixture is 100% stoichiometric. The percentage stoichiometric diminishes or increases as the mixture is weakened or enriched. Thus for example a mixture 20% weak is 80% of stoichiometric and one 20% rich is 120% of stoichiometric.

The terms Compression Ratio, Mixture Strength, Indicated Thermal Efficiency, and Indicated Mean Effective Pressure are, when convenient, abbreviated to C.R., M.S., I.T.E., and I.M.E.P. respectively. Values of C.R. are given as single numbers. A stoichiometric mixture is described as "correct" in the text; the abbreviation C.C.M. is used on the graphs. It is to be understood that numerical values given on graphs for I.M.E.P. and Engine Speed are in pounds per square inch (p.s.i.) and revolutions per minute (r.p.m.) respectively.

I. THE IGNITING EFFECT OF THE CERAMIC CORE OF A SPARK PLUG

Preliminary Experiments

The operating conditions were similar to those in which some degree of preignition occurred in the course of the experiments described in Part V (12) when a correct hydrogen-air mixture was used at a C.R. of 10, with the

jacket coolant at 212°F. and the mixture supplied at room temperature. A C.F.R.-8 spark plug which is a "hot" variety was used, the exhaust valve was of silchrome steel, uncooled, and the inlet valve was of the shrouded type which provided a swirl in the entering mixture. Thus the conditions were essentially those used for the knock rating of fuels by the C.F.R.-A.S.T.M. motor method.

The experiments were carried out with the C.R. fixed at 10, with engine speeds of 600, 900, 1200, and 1500 r.p.m. while mixtures were varied from very weak to extremely rich. The results obtained for the relation between I.H.P. and M.S. are given by the graphs of Fig. 1.

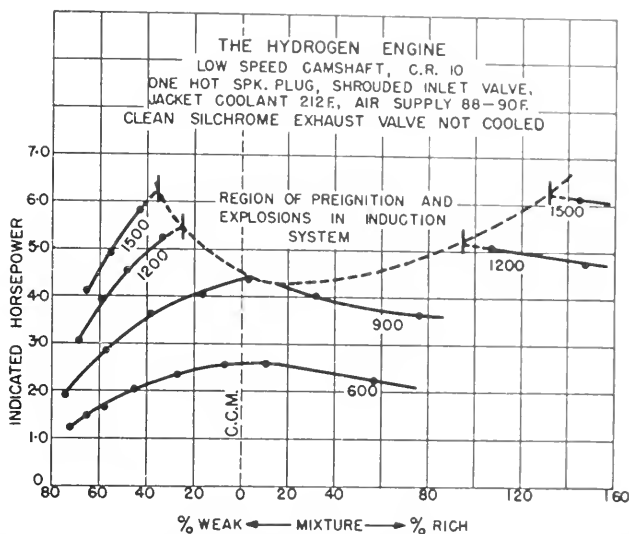


FIG. 1. Mixture strengths over which premature ignition occurs when engines speeds exceed 900 r.p.m. and a C.F.R.-8 spark plug, a hot variety, is used in the standard position.

It will be seen by reference to the graphs that at 600 r.p.m. a maximum value of 2.6 was obtained for I.H.P. when the mixture was 10% rich. There was no preignition. When however the heat load was increased by raising the speed to 900 r.p.m. and I.H.P. attained a maximum of 4.3, there was some degree of preignition but not enough to interrupt the experiment. This result was similar to that obtained in similar conditions as described in Part V (12). Then when the heat load was further increased by raising the speed to 1200 and then to 1500 r.p.m. the range of M.S. over which running was impossible, because of backfiring into the induction system, increased as shown by the relevant graphs. Thus at 1500 r.p.m. backfiring occurred over the mixture range 40% weak to 140% rich.

Ignition by a Hot Spark Plug without a Central Electrode

Preignition is frequently attributed to the central electrode of the spark plug becoming overheated. Pye (15, p. 91), for example, mentions only the

central electrode and scraps of incandescent carbon; Hundere and Bert (6, p. 553), fragments *detached* from the ceramic core. The experiments described in Part XXVI (10) indicated that preignition would preferably be initiated by the surface of the ceramic core of the spark plug even if its temperature were not higher than that of other surfaces in the combustion chamber.

Experiments were carried out accordingly in the operating conditions used for the preliminary experiments but with the mixture fired by a cool variety of spark plug, a K.L.G.-100, in the standard position while a standard but unfired hot variety, a C.F.R.-8, was in the No. 2 position. The central electrode of this plug had been cut off. The standard and the No. 2 positions are shown by Fig. 2. It will be seen by reference to the figure that the swirl due to the

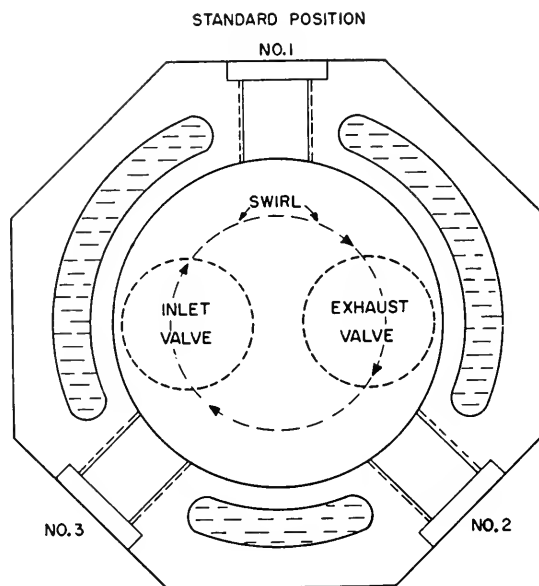


FIG. 2. Location of spark plug holes in wall of the combustion chamber and the mixture swirl due to the use of the C.F.R. shrouded inlet valve.

shrouded inlet valve directs the relatively cool entering mixture over the spark plug in the standard position and that it then passes over the hot exhaust valve before arriving at the unfired plug in the No. 2 position.

The experimental results obtained for the relation between I.H.P. and M.S. with speeds of 600, 900, 1200, and 1500 r.p.m. are given by the graphs of Fig. 3. It was just possible to use the maximum power mixture strength without the occurrence of preignition at the low speed of 600 r.p.m., the corresponding maximum I.H.P. being 2.6. Then on raising the speed to 900 r.p.m. preignition accompanied by backfiring occurred with mixtures ranging from 16% weak to 67% rich and the range of mixture strength over which running was impossible increased as speed and the corresponding heat load were further increased, as illustrated by the graphs of the figure.

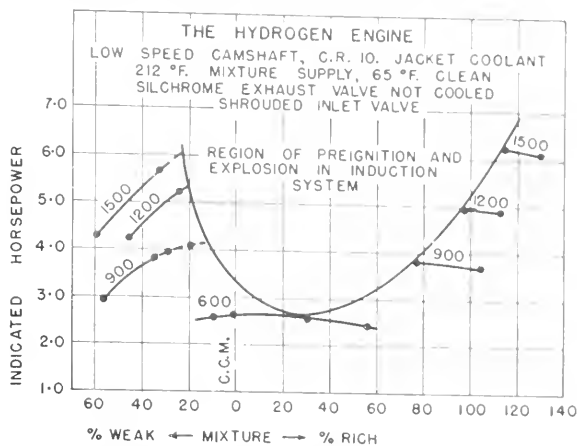


FIG. 3. Mixture strengths over which premature ignition occurs at engine speeds exceeding 600 r.p.m. when an unfired hot spark plug without projecting central electrode is in No. 2 position and ignition is by a cool spark plug in the standard position.

II. THE LIMITATION OF POWER AND ECONOMY BY THE ONSET OF PREIGNITION DUE TO THE ATTAINMENT OF AN IGNITING TEMPERATURE BY THE CERAMIC CORE OF THE SPARK PLUG

The experiments described in Section I were carried out at a C.R. of 10 and in the absence of an accumulation of finely divided carbon in the combustion chamber. The maximum power attainable was limited by preignition arising from the ceramic core of the C.F.R.-8 spark plug having attained an igniting temperature in respect of the hydrogen-air mixture. Moreover it was shown by the experiments with combustion tubes (Part XXVI (10)) that a correct mixture would be ignited by the exhaust valve if it attained a temperature of approximately 1100°F. It was decided accordingly to use a sodium cooled valve for further experiments and to maintain the jacket coolant at 100°F. and the entering mixture at 65°F. The shrouded inlet valve was replaced by a plain type although this led to an increase in volumetric efficiency and consequently to an increase in heat load. The volumetric efficiency at high speeds was however restricted to some extent by the continued use of the low speed camshaft. The object of the changes mentioned was to ensure that preignition, when it occurred, was due solely to the temperature attained by the ceramic core of the spark plug. Experiments were carried out at a C.R. of 10 and with speeds of 900, 1200, 1500, and 1800 r.p.m. when a hot spark plug was used and repeated after a change to a cool variety of spark plug.

Hot Spark Plug Experiments

A Champion C.F.R.-8 was used as a hot plug. The relation between I.H.P. and the values of M.S. that could be used before the experiment was interrupted by the occurrence of preignition and backfiring is given by the *A* graphs of Fig. 4, for the four engine speeds. Backfiring began on increasing M.S. to the values shown by the short vertical lines of the graphs. The mixture was then 42% weak at speeds of 1500 and 1800 and 38% weak at 900 and 1200. A value

of 40% weak, taken irrespective of engine speed, would be within experimental accuracy. Preignition and backfiring did not occur when extremely rich mixtures were used. The values then obtained for I.H.P. are not given by the graphs. The small ranges of M.S. usable in the conditions of the experiments included the weak value for which indicated thermal efficiency was a maximum. Relevant data are tabulated below.

TABLE 1

MIXTURE STRENGTH FOR MAXIMUM I.T.E., 60% WEAK
ONE HOT SPARK PLUG, LOW SPEED CAMSHAFT, C.R. 10.0

Speed	Opt. spk. Advance	I.M.E.P.	I.T.E. %
1800	30°	80	43.0
1500	32°	81	43.5
1200	32°	81	43.0
900	32°	80	41.5

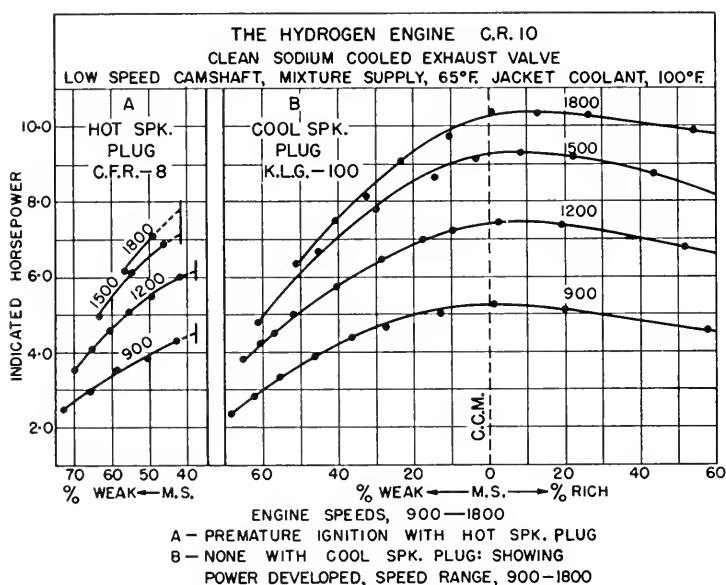


FIG. 4. Graphs A and B illustrate the effect of changing from a hot to a cool variety of spark plug; other running conditions having remained unchanged.

Cool Spark Plug Experiments

A K.L.G. 100 was used as a cool plug. The relation between I.H.P. and M.S. then obtained without otherwise changing conditions of experiment is given by the B graphs of Fig. 4. They show that a remarkable effect, which prevented premature ignition, had been obtained. Thus referring to the figure it will be

seen that hydrogen-air mixtures ranging from 70% weak to 80% rich were used at speeds ranging from 900 to 1800.

The values obtained for I.T.E. and I.M.E.P. when the M.S. was used for maximum power and optimum spark timing are given, in Table II, below. Maximum power was always obtained when using a mixture 5% rich. The values for I.T.E. and the corresponding values of I.M.E.P. obtained when using the M.S. for maximum I.T.E. are given in Table III.

TABLE II
MIXTURE STRENGTH FOR MAXIMUM POWER, 5% RICH
ONE COOL SPARK PLUG, LOW SPEED CAMSHAFT, C.R. 10

Speed, r.p.m.	% Vol. eff.	Spk. timing	I.H.P.	I.M.E.P.	I.T.E.
1800	77	1° adv.	10.4	123	36
1500	84	t.d.c.	9.3	132	35
1200	86	1° ret'd	7.6	134	35
900	86	1° ret'd	5.4	126	33

TABLE III
MIXTURE STRENGTH FOR MAXIMUM THERMAL EFFICIENCY, 55% WEAK
ONE COOL SPARK PLUG, LOW SPEED CAMSHAFT, C.R. 10

Speed, r.p.m.	% Vol. eff.	Spk. adv.	I.H.P.	I.M.E.P.	I.T.E.
1800	75	35°	6.1	75	43.6
1500	85	26°	6.0	85	41.0
1200	91	28°	4.9	87	42.4
900	91	22°	3.6	85	42.0

It is shown by the data of Tables II and III that a maximum value of 134 was obtained for I.M.E.P. with a speed of 1200 and the somewhat lower value of 132 on increasing speed to 1500. A maximum of 42.4% was obtained for I.T.E. with a speed of 1200 and of 44% on increasing the speed to 1500. The I.H.P. obtained with the maximum lower mixture increased from 4.9 to 6.0 on increasing the speed from 1200 to 1500 but an increase to 6.1 only was obtained on further increasing speed to 1800 and the I.M.E.P. decreased from 132 to 123.

It is evident that the valve timing provided by the low speed camshaft was suitable for use at speeds of from 1200 to 1500 but not for a speed of 1800. Comprehensive performance data were obtained for the four speeds used for the experiments and with mixtures ranging from 66% weak to 60% rich. The data are given by the graphs of Fig. 5 for a speed of 1500 only.

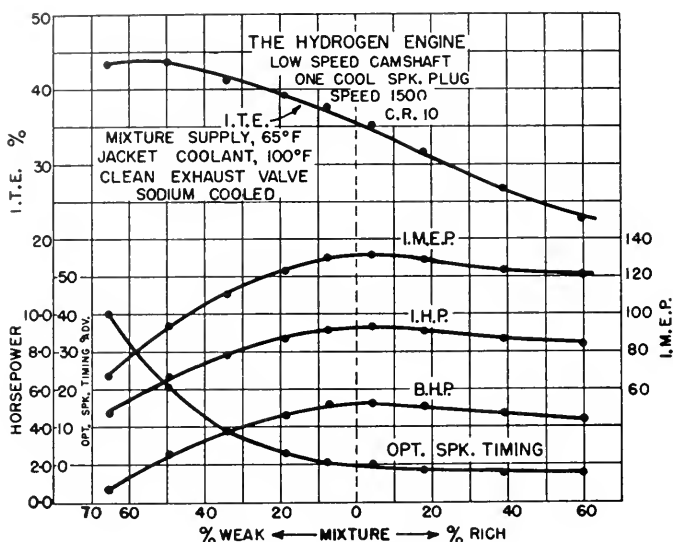


FIG. 5. Performance data, mixtures 66% weak to 60% rich, obtained when ignition is by a cool spark plug, speed 1500 r.p.m. and C.R. 10:1.

III. THE MEAN TEMPERATURES ATTAINED BY HOT AND COOL SPARK PLUG CORES, AN UNCOOLED EXHAUST VALVE, AND THE EXHAUST GAS, AS AFFECTED BY MIXTURE STRENGTH

The experiments were carried out with an engine speed of 1200 r.p.m., a C.R. of 10, temperatures of jacket coolant and mixture supply 100° and 65°F. respectively. The experimental results are given by the graphs of Fig. 6.

The C.F.R.-8 Spark Plug

The spark plug with a thermocouple in the central electrode near the tip of the ceramic core was supplied by the Champion Spark Plug Company. Thus the temperature at that position could be measured while the spark plug, placed in the standard position, was used to fire the hydrogen-air mixture. The temperatures attained as M.S. was increased from 70% weak are given by the *A* graph of the figure. Preignition occurred on increasing the M.S. to 33% weak. A temperature of 1150°F. had then been attained at the position of the thermocouple.

The Uncooled Exhaust Valve

The valve was of silchrome steel, supplied as standard for the C.F.R.-A.S.T.M. motor method of knock rating. It was obtained with the stem drilled for a thermocouple to be fitted in a manner suitable for the measurement of the temperature of the exposed surface. The temperatures thus measured while ignition was provided by a cool spark plug, a K.L.G. 100, in the standard position, are given by the *B* graph of the figure. It will be seen that the temperature of the exhaust valve rose from 590° to a maximum of 1150°F. as M.S. was increased from 66% weak to 5% rich. There was no preignition.

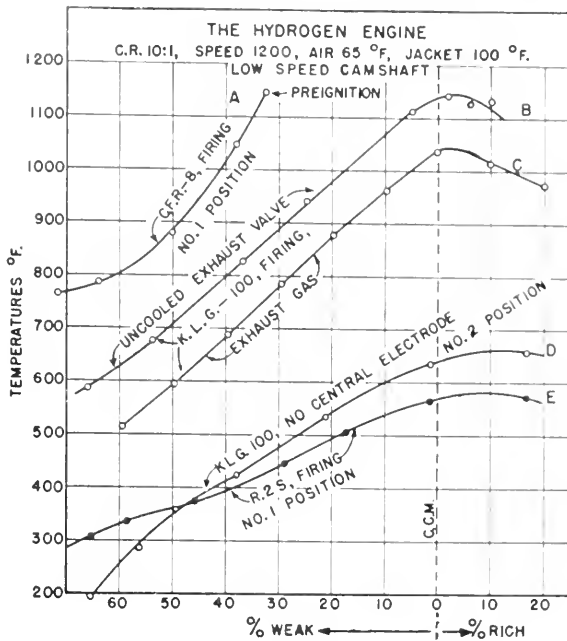


FIG. 6. Mixture strength and the corresponding temperatures of an uncooled exhaust valve, the exhaust gas, and hot and cool spark plugs.

The Exhaust Gas

The temperature was measured by using a bare thermocouple placed in the exhaust system approximately 3 in. from the valve. The temperatures thus measured, as M.S. was increased from 60% weak to 20% rich, are given by the *C* graph of the figure. They were measured at the same time as those of the uncooled exhaust valve. It will be noted that the temperature of the uncooled exhaust valve was always higher than that of the exhaust gas. The temperature of a sodium cooled valve in an air cooled cylinder was always lower than that of the exhaust gas, according to experiments by Sanders, Wilstead, and Mulcahy (17).

The Cool Spark Plugs, R2-S and K.L.G. -100

An R2-S spark plug with a thermocouple in the central electrode near the top of the ceramic core was placed in the standard position and used for firing the mixture. A K.L.G.-100 was prepared for the experiments by removing the central electrode and replacing it by a thermocouple cemented in at about 1/8 in. from the tip of the ceramic core. This plug was placed in the No. 2 position. The inlet valve was of the plain type, thus there was no swirl to influence the relative temperatures attained by the spark plugs. The K.L.G. plug in the No. 2 position was however closer to the exhaust valve than the champion plug in the standard positions. The temperatures, as measured while M.S. was increased from 70% weak to 20% rich, are given by graphs *D* and *E* of the figure. It will be seen that the temperatures attained by the two

plugs did not differ to a significant extent, allowing for their relative positions, and that the maximum temperature of 670°F., which was attained with a mixture 10% rich by the K.L.G.-100 plug, is far below that required for the ignition of any hydrogen-air mixture.

IV. THE LIMITATION OF POWER AND THERMAL EFFICIENCY BY THE ONSET OF PREIGNITION DUE TO THE EXHAUST VALVE HAVING ATTAINED AN IGNITING TEMPERATURE

The experiments described in Sections II and III demonstrated that pre-ignition due to the ceramic core of the spark or to its central electrode did not occur when a cool type of spark plug was used. It was shown however, by the *B* graph of Fig. 6, that the temperature attained by the exhaust valve approached the value required for the ignition of a correct hydrogen-air mixture when the engine speed was 1200 r.p.m. and the C.R. 10:1. It appeared therefore that preignition by the exhaust valve might become a limiting factor in respect of power and thermal efficiency on raising the heat load.

Experiments were therefore carried out in the operating conditions used for those described in Sections II and III, except that volumetric efficiency and the consequent heat load were increased by using a "high speed" camshaft. There was then a corresponding increase in the temperature of the exhaust valve and a further increase due to the valve lift being increased from 0.238 in. to 0.312 in. and to the time the valve was off its cooling seat being increased from 145° to 155° of crank revolution. The values for I.H.P. obtained with mixtures ranging from 70% weak to 60% rich are given by the graphs of Fig. 7. The I.H.P. attained a maximum of 11.0 with a speed of 1800 r.p.m. as compared with the value of 10.4 obtained when using the low speed camshaft,

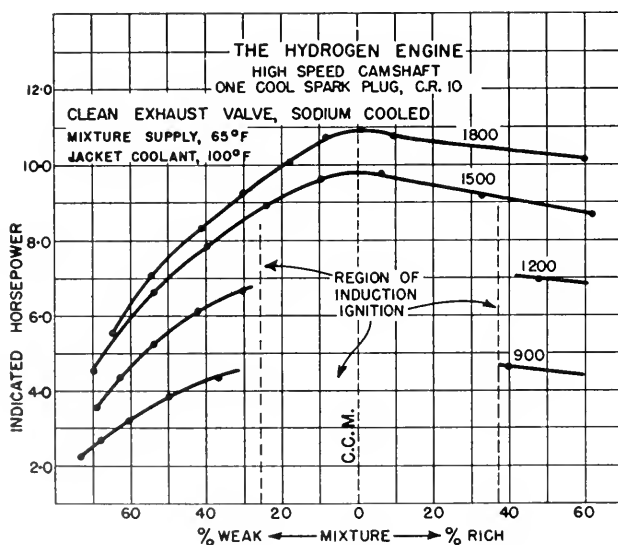


FIG. 7. Premature ignition at speeds lower than 1500 r.p.m. as obtained when changing to the high speed camshaft, other running conditions remaining unchanged.

Fig. 4. The especially noteworthy feature of the experiments was that preignition and backfiring into the induction system occurred when speed was *reduced*.

An explanation was provided by the results of the experiments with steel combustion tubes, Part XXVI (10). It was found in these experiments that the igniting effect of a clean stainless steel surface was reduced if it was aged by exposure at high temperatures to hydrogen air mixtures for the time required for the formation of an adherent layer of oxide. Moreover it was shown that the difference in the igniting effects increased as time of exposure to hydrogen-air mixtures was increased. Thus it would be expected that in the engine an exhaust valve with a clean surface would ignite a hydrogen air mixture at a lower temperature than would be required by one with an aged surface and that the difference in the igniting effects would increase on decreasing the engine speed.

The surface of the exhaust valve had always been cleaned with abrasive material for the experiments described earlier in this Part but in view of the results of the experiments with stainless steel combustion tubes the clean exhaust valve was replaced by a similar sodium cooled valve which had been put aside after having been used for a long period during which a coating of oxide had formed. The valve is described accordingly as "aged".

The engine then ran at speeds ranging from 900 to 1800 r.p.m. with an entire absence of preignition. No alteration other than the change of exhaust valves had been made in the operating conditions. The values obtained for I.H.P. when mixtures ranging from 70% weak to 70% rich were used are given by the graphs of Fig. 8. The experiments were of a preliminary nature made to verify that preignition would be avoided by using an aged instead of an initially clean exhaust valve.

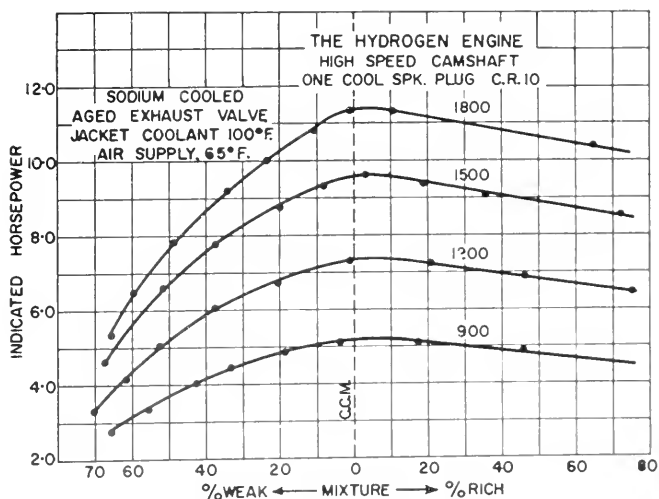


FIG. 8. Graphs showing the absence of low speed premature ignition when the exhaust valve was aged.

Performance Data for Six Engine Speeds

Further experiments were carried out to obtain complete performance data when the aged exhaust valve was used with speeds of 1100 and 1300 r.p.m. in addition to the speeds of 900, 1200, 1500, and 1800 r.p.m., while mixtures were varied from 70% weak to 70% rich. The data obtained when the mixtures required for maximum I.H.P. and maximum I.T.E. were used are tabulated in Tables IV and V, respectively.

TABLE IV

MIXTURE STRENGTH FOR MAXIMUM POWER; AGED EXHAUST VALVE
HIGH SPEED CAMSHAFT, ONE COOL SPARK PLUG, C.R. 10

Speed	% Vol. eff.	Spk. timing	M.S.	I.H.P.	I.M.E.P.	I.T.E. %
1800	81.1	2° adv.	5% rich	11.40	135	36.5
1500	89.6	t.d.c.	5% rich	9.65	139	35.0
1300	89.0	t.d.c.	7% rich	8.05	132	34.5
1200	90.6	t.d.c.	6% rich	7.40	131	34.0
1100	87.8	t.d.c.	6% rich	6.60	128	33.5
900	84.5	2° retard	5% rich	5.25	122	33.0

TABLE V

MIXTURE STRENGTH FOR MAXIMUM INDICATED THERMAL EFFICIENCY, 55% WEAK;
AGED EXHAUST VALVE
HIGH SPEED CAMSHAFT, ONE COOL SPARK PLUG, C.R. 10

Speed	% Vol. eff.	Spk. adv.	I.H.P.	I.M.E.P.	I.T.E. %
1800	83	24°	7.0	83	44.4
1500	87	27°	6.1	87	43.2
1300	84	30°	5.1	84	42.0
1200	84	31°	4.8	84	41.5
1100	82	30°	4.2	82	41.5
900	80	30°	3.3	80	40.2

It will be seen by reference to Table IV that I.H.P. was 11.4 at 1800 r.p.m., as compared with 10.4 H.P. obtained when the low speed camshaft was used, see Table II. The maximum values for I.M.E.P. and volumetric efficiency were obtained at 1500, indicating that the valve timing provided by the high speed camshaft was most suitable for that engine speed provided that preignition was avoided by using an aged exhaust valve. The I.M.E.P. was then 139 as compared with a value of 132 p.s.i. obtained when the low speed camshaft and a speed of 1500 was used, and 134 when the speed was 1200 r.p.m. It may be concluded that in so far as I.M.E.P. is concerned, the valve timing provided by the low speed camshaft is most suitable for an engine speed of 1200 and that provided by the high speed camshaft is best for an engine speed of 1500 r.p.m.

The maximum values for I.T.E. were always obtained when the mixtures were 55% weak, when either the low or the high speed camshaft was used.

The values obtained with the low speed camshaft, Table III, increased from 42% at a speed of 900 to attain a maximum of 41% at 1500 r.p.m. and a lower value of 43.6% at 1800 r.p.m. On the other hand the values obtained when the high speed camshaft was used increased with fair regularity from a low of 40.2% at 900 to a maximum of 41.4% at 1800 r.p.m., Table V. Performance data for mixtures ranging from 70% weak to 80% rich are given by the graphs of Fig. 9 for the engine speed of 1500 at which a maximum of 139 was obtained for I.M.E.P.

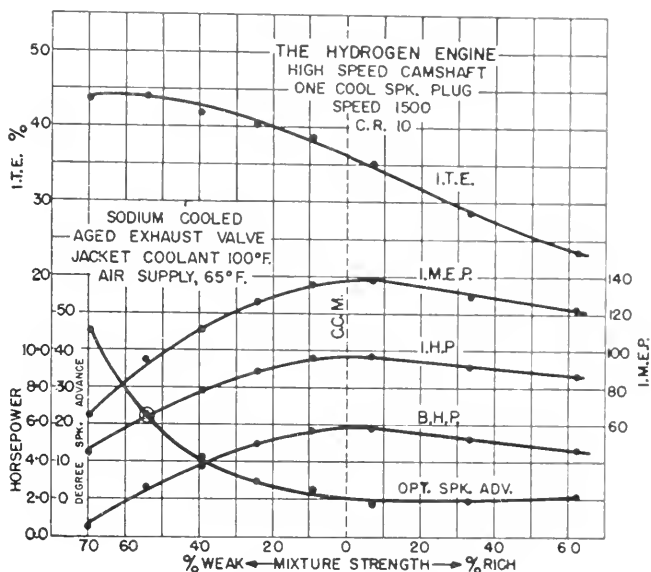


FIG. 9. Performance data, mixtures 70% weak to 60% rich, obtained when using the high speed camshaft and the aged exhaust valve. Speed 1500 r.p.m. C.R. 10:1.

Indicator Diagrams

The indicator diagrams, Fig. 10, were taken when a Draper-Li pressure pickup was used. The pressure scale is linear and maximum values in pounds per square inch are given by the calibration marks on the diagrams. The diagrams were taken when a C.R. of 10 was used and when, under the operating conditions used, the performance data given in Tables IV and V were obtained, at an engine speed of 1500 r.p.m.

The pressure waves started by the spark are most pronounced, when with mixtures nearly correct the pressure rise due to combustion began immediately after its passage, diagrams *A* and *B*. Spark timing is shown on the diagrams by small rather faint blips fed into the electronic circuit. These are marked by arrows. Similar blips marked by short vertical lines were fed into the circuit at t.d.c. and at intervals of 10° for 30° before and after.

Spark timing was always adjusted to obtain maximum power output and it will be noted that maximum combustion pressure then occurred at approxi-

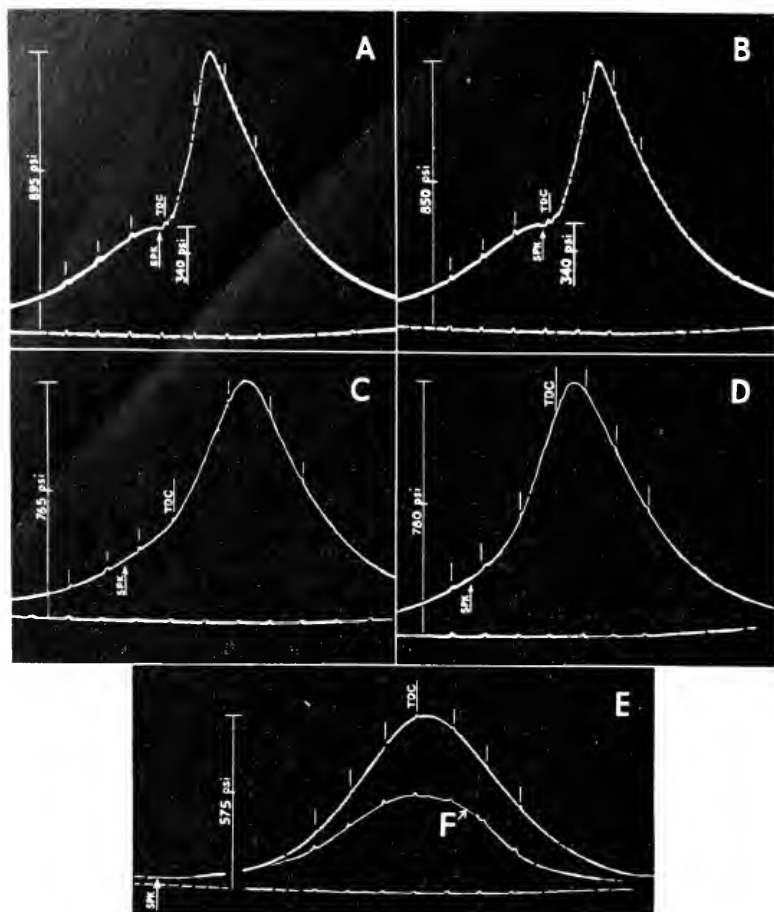


FIG. 10. Pressure-time diagrams taken with a Draper-Li pressure pickup. C.R. 10:1 speed 1500 r.p.m.

A, M.S. 3% rich, spk. 1° retard.
C, M.S. 34% weak, spk. 14° adv.
E, M.S. 80% weak, spk. 75° adv.

B, M.S. 8% weak, spk. 1° adv.
D, M.S. 50% weak, spk. 25° adv.
F, air only.

mately 15° after t.d.c. when the mixture was nearly correct, diagrams *A* and *B*, but at approximately 5° after t.d.c. when mixtures 34, 50, and 80% weak were used, diagrams *C*, *D*, and *E*.

The power developed with a mixture 80% weak was insufficient to overcome friction and pumping losses and the speed of 1500 r.p.m. was maintained by partial motoring of the engine. Diagram *F*, shown below diagram *E*, was taken when air only was supplied to the engine. The pressures shown accordingly can be used for estimating the approximate combustion pressures obtained when mixtures with hydrogen were used.

The diagrams show that if lubricating oil passed into the combustion chamber at the minimum rate practicable, the rate of burning of a hydrogen-air mixture 5% rich or 8% weak was such that its combustion required a time

represented by nearly 15° of crank revolution and that *autoignition did not occur even when the compression ratio was 10:1.*

V. OPERATION OF THE ENGINE AT 12:1 COMPRESSION RATIO

The controllable operating conditions were as had been used at a C.R. of 10, as described in Section IV, except that the temperature of the jacket coolant was reduced from 100° to 65°F . An unavoidable change in conditions occurred on raising the C.R. to 12:1, in that the top piston ring then lost its bearing on the cylinder wall at the three spark plug holes. Moreover a larger pocket into which lubricating oil could leak past the piston was formed between the end of the spark plug and the top piston ring than between the ends of the two blank plugs and the piston ring.

The operation of the engine at a C.R. of 12 and a speed of 1800 r.p.m. in the conditions described was accompanied by some degree of preignition which occurred occasionally only and did not lead to backfiring. When however volumetric efficiency was increased by reducing the speed to 1500 r.p.m., preignition occurred occasionally with a mixture 5% rich, frequently with one 30% rich, and developed into backfiring with a mixture 80% rich.

The engine was then dismantled for inspection and cleaning of the combustion chamber. Patches of soot, easily wiped off, were found on the piston crown adjacent to the three spark plug holes. The patch adjacent to the spark plug hole was larger than those adjacent to the two holes occupied by blank plugs. Similar patches of soot were not found when the engine was dismantled after running at a C.R. of 10.

Method of Avoiding Preignition by Lubricating Oil Soot and the Consequent Improvement in Engine Performance

The extent of the deposits of soot on surfaces in the combustion chamber was found to depend on the time of running required for the accumulation of a quantity of lubricating oil in the pockets provided by the spark plug holes. Thus starting with a weak mixture and taking the observations required for performance data as rapidly as possible, it was found that preignition did not occur until a mixture richer than correct was used. When a mixture 10% weak was again used and the engine run for 10 to 15 min., the excess soot on the piston crown burned off and observations for performance data for the richer mixture without interruption by preignition were obtained. With this procedure, performance data were obtained for mixtures ranging from 70% weak to 80% rich and, in the absence of preignition, higher values for power and thermal efficiency were obtained than when experiments had been interrupted by preignition and backfiring.

Values for I.H.P. obtained at speeds of 1200, 1500, and 1800 r.p.m. and with hydrogen-air mixtures ranging from 70% weak to 80% rich are given by the graphs of Fig. 11.

Values for I.H.P., B.H.P., I.M.E.P., I.T.E., and opt. spark timing are given for a speed of 1500 with mixtures ranging from 70% weak to 80% rich, by the graphs of Fig. 12.

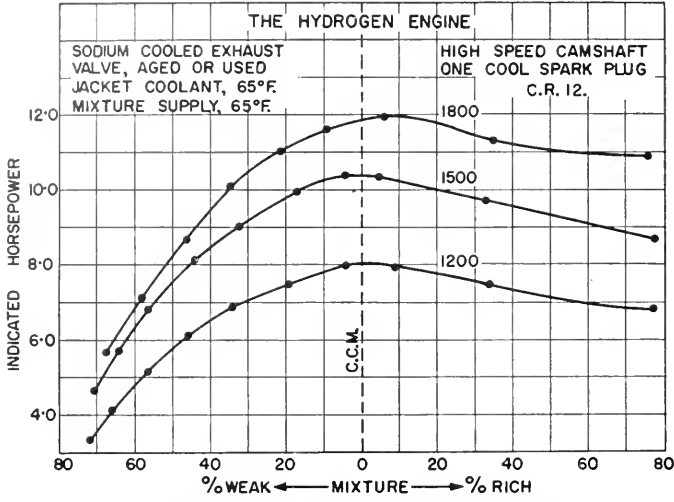


FIG. 11. Power developed at 12:1 C.R. on reducing the concentration of soot derived from pyrolysis of the vapor of excess lubricating oil and thus avoiding nuclear ignition.

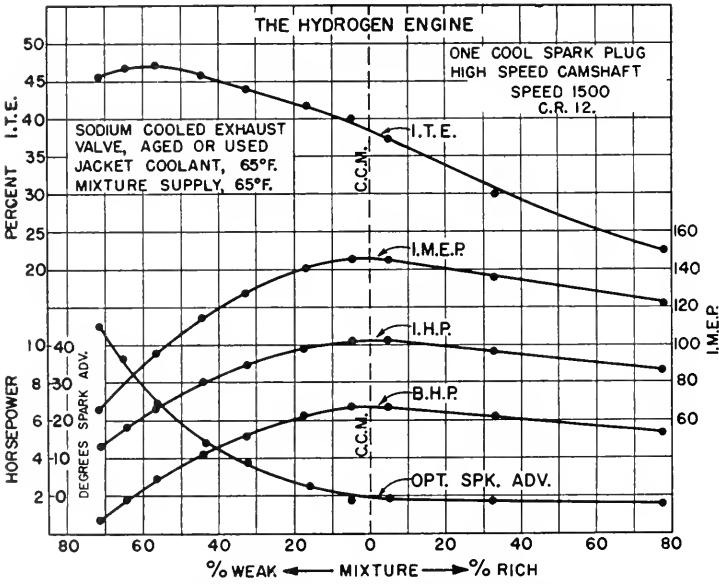


FIG. 12. Performance data obtained in the absence of nuclear ignition when using mixtures 70% weak to 80% rich at 1500 r.p.m. and a C.R. of 12:1.

Performance data obtained when the mixture strength was that required for maximum power and that required for maximum indicated thermal efficiency are of especial interest and are given in Tables VI and VII respectively. Values of opt. spark timing and volumetric efficiency are also given.

It will be seen by references to the tables that a maximum of 146 p.s.i. was obtained for I.M.E.P. when the engine was operated at 1500 r.p.m. and

TABLE VI

MIXTURE STRENGTH FOR MAXIMUM POWER; AGED OR CLEAN EXHAUST VALVE
HIGH SPEED CAMSHAFT, ONE COOL SPARK PLUG, COMPRESSION RATIO 12:1

Speed, r.p.m.	% Vol. eff.	Spark timing	I.H.P.	I.M.E.P.	I.T.E. %
1800	85.4	1° retard	11.9	140	37
1500	89	1° retard	10.3	116	37
1200	87.3	2° retard	8.0	111	36

TABLE VII

MIXTURE STRENGTH FOR MAXIMUM INDICATED THERMAL EFFICIENCY;
AGED OR CLEAN EXHAUST VALVE
HIGH SPEED CAMSHAFT, ONE COOL SPARK PLUG, COMPRESSION RATIO 12:1

Speed, r.p.m.	% Vol. eff.	Spark timing	I.H.P.	I.M.E.P.	I.T.E. %
1800	83.7	25° adv.	7.6	90	47
1500	91.5	25° adv.	6.9	96	47
1200	91	27° adv.	5.3	91	41

that a maximum of 47% was obtained for I.T.E. when the engine was operated at 1800 r.p.m. Values of 47½% were not uncommon but are not shown on the relevant graph of Fig. 12.

Lubricating oil always passed the piston at an abnormal rate when the C.R. was raised to 12. There was therefore always an appreciable concentration of lubricating oil vapor in the compressed hydrogen-air mixture. The pyrolysis of this vapor produced the finely divided carbon which remained in part as soot on the piston crown and required removal by the method described in order to avoid preignition. In these circumstances the difference in the igniting effect due to the exhaust valve being aged or initially clean was masked by the nuclear igniting effect.

The procedure adopted to obtain performance data with a hydrogen-air mixture at a C.R. of 12 was made necessary by the particular design of the C.F.R. cylinder and piston. It could therefore be changed in a manner such that experiments could be carried out at compression ratios higher than 12:1. Thus we have, by limiting the time during which oil passed the piston, been able to operate for a short period at a C.R. of 16:1 with a maximum power mixture.

DISCUSSION

Hydrogen either free or in combination with carbon is a constituent of the gases or liquids commonly used as engine fuels. The characteristics of the combustion of hydrogen only should therefore be of fundamental significance. It seems however to have long been accepted that hydrogen cannot be used as the sole fuel, because of the occurrence of premature ignition, in the operating conditions required to obtain optimum values for power output and the corresponding thermal efficiency.

Lucke (14, 1906) states that "Gases rich in hydrogen *preignite easily* and that approximately one atmosphere should be deducted from the compression pressure allowable with no hydrogen for each 5% of hydrogen present". Tizard (19, p. 22, 1921) states that "Hydrogen *detonates easily* in an internal combustion engine, at quite low compression ratios, but nevertheless it has a high ignition temperature". Ricardo (16, pp. 334-337, 1922), with the E35 engine operated at 1500 r.p.m., found that it was possible to use a nearly correct hydrogen-air mixture at a compression ratio of 5.45:1, but "if an attempt was made to use a rich mixture, violent *preignition* occurred, accompanied by firing back into the carburetor, which rendered further running impossible. Even with the compression ratio lowered to 3.8:1, the same thing occurred". Burstall (2, 1927) operating another E35 engine, at 1000 r.p.m. and compression ratios of 5 and 7:1, found that "The experimental range (of mixture strength) which can be used with hydrogen is strictly limited by its readiness to *detonate*, both at high compression ratios and with rich mixtures, and even more by its tendency to backfire with mixtures richer than 20% weak at a compression ratio of 5:1". Premature ignition, described as *detonation*, was obtained by Egerton, Smith, and Ubbelohde when they were using an ethyl knock testing engine (5, 1935). The effect was attributed at the time to nitrogen peroxide formed from the nitrogen of the air, but some years later to *preignition* (4, p. 917, 1949).

Downs, Walsh, and Wheeler (3, p. 517, 1951), as a result of experiments with hydrogen as the fuel for a Ricardo E6 engine, state that "In most cases, owing to the *extreme ease with which it ignites*, a mixture richer than about 25 to 30% weaker than chemically correct cannot be used. If the attempt is made to run with a richer mixture, *self-ignition* occurs so early in the compression stroke that the mixture is eventually ignited in the induction manifold". The statement that hydrogen-air mixtures "ignite with extreme ease" cannot be accepted as fact. Reference was made to the finding of King, Wallace, and Mahapatra that, by keeping the combustion chamber as clean as possible, the engine could be operated over the whole mixture range without backfiring (12). It was not mentioned that this occurred at a compression ratio of 10:1 and a speed of 900 r.p.m. The reference is also misleading in that it should have been to fluffy carbon that accumulated in an initially clean combustion chamber as described on page 269 of reference (12). Moreover it was not mentioned that preignition and backfiring occurred when charcoal dust was added to the mixture supplied to the engine. Although Ricardo's early statement regarding the impossibility of using rich mixtures is echoed, they describe the premature ignition as "*self-ignition*" instead of by the term *preignition* used by Ricardo. Self-ignition was treated as detonation and attributed to a chain reaction mechanism to be described in a subsequent publication.

Anzilotti and associates (1, 1954) describe experiments with a C.F.R. engine operated at 900 r.p.m. with a jacket coolant temperature of 212°F. and an inlet mixture temperature of 100°F. The results obtained were similar to those of Downs, Walsh, and Wheeler (3) in that, when the mixture strength re-

quired for maximum power was used, the highest compression ratio usable without knock was approximately 8:1. It is stated that the "knock" was similar to that obtained with paraffinic fuels and was attributed to the chain reaction mechanism devised by Lewis and Von Elbe to explain the autoignition of *hydrogen-oxygen* mixtures. In our preliminary experiments also carried out with a similar engine and operating conditions but with a combustion chamber initially clean, the knock limited compression ratio was 10:1 when a nearly correct mixture was used (see Fig. 1, this Part) and it was shown by subsequent experiments described in Section I to have been due at 900 r.p.m. to the ceramic core of the spark plug having attained an igniting temperature.

Livengood and Leary (13) obtained what appeared to be autoignition of a correct hydrogen-air mixture when using the compression ignition machine developed by C. F. Taylor and associates (18). The compression ratio was 12:1 and after nearly adiabatic compression the mixture was held against the thick plate glass window which formed the cylinder head until ignition occurred after a few milliseconds. The window was used for photographic recording of the process of ignition and therefore was not cooled. In view of the experiments described in Section III in which a mixture 33% weak was ignited by the surface of the ceramic core of a spark plug at a compression ratio of 10:1, it may safely be assumed that the ignition observed by Livengood and Leary occurred because a layer of molecules on the surface of the uncooled plate glass window attained the required temperature. Thus it was observed by them that "all mixtures give off a bright yellow light during autoignition. When specimen inflammations were examined with a spectrograph, the presence of a strong sodium-D line was revealed in each instance". Efforts were made to find and eliminate the source of the sodium but apparently it was not realized that it could be provided by the plate glass. In spite of their efforts, "all fuels including hydrogen, continued to emit the characteristic yellow light".

The experiments described in this Part show clearly that optimum performance in terms of power and economy is limited only by preignition arising from the temperature attained by the ceramic core of the spark plug or by the exhaust valve or from nuclei formed by pyrolysis of lubricating oil vapor. It was shown by indicator diagrams that detonation, defined as auto or self ignition, did not occur in the absence of nuclei of ignition.

On reducing the magnitude of the igniting effects mentioned it became possible to operate the engine at speeds rising to 1800 r.p.m., with the compression ratio fixed at 12:1. Values of 146 p.s.i. for I.M.E.P. and of 37% for I.T.E. were obtained when the maximum power mixture strength was used. The values obtained with a mixture 55% weak were 90 p.s.i. for I.M.E.P. and 47% for I.T.E. These values exceed those recorded in the literature of the subject, by a wide margin.

ACKNOWLEDGMENTS

The experiments described in this Part were carried out in the Department of Mechanical Engineering, University of Toronto, with the co-operation of

Professor E. A. Allcut, Head of the Department, the assistance of Mr. S. V. Hayes, Scientific Officer Defence Research Board, and that of Joseph Thurner, Technician. Acknowledgment is also made of the assistance with preliminary experiments given by Professor Bernard D. Wood, Department of Mechanical Engineering, University of Manitoba.

The Consumers Gas Company, Toronto, contributed to the experimental work by providing facilities under the direction of Mr. J. Alex Morrison for the calibration of hydrogen metering orifices; the Champion Spark Plug Company, by supplying spark plugs with thermocouples in the central electrodes; The Eaton Manufacturing Company, Detroit, by supplying a silchrome valve with the stem drilled for leads to a thermocouple in the head.

The Authors are indebted to the Chairman of the Defence Research Board for permission to publish this paper.

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APPENDIX

Metering of Hydrogen Supply

Accurate measurement of rate of hydrogen supply to the engine is of prime importance in respect of determinations of thermal efficiency. The novel method used for the experiments was based on the use of two calibrated square edged orifices in thin plates. One was 0.1286 in. and the other 0.0784 in. diameter. The plates were 0.013 in. thick. The orifices were mounted midway in brass tubes 4 in. diameter and 4 ft. long provided with baffles and wire mesh screens for the elimination of pressure pulsations from the induction system of the engine. The double system of hydrogen supply to the engine through

small orifices of different diameters, which could be used singly or in parallel, was such that hydrogen could be supplied at rates required for the experiments while the velocity of flow through a metering orifice was never less than 750 ft. per sec. This feature in conjunction with the means taken to eliminate pressure fluctuations made possible the use of orifice calibrations determined in steady flow conditions.

The orifices, in position in the tube mountings, were calibrated in the Meter Testing Department of the Consumer's Gas Company, Toronto, under the direction of Mr. J. Alex Morrison, Supervisor of the Appliance Laboratory. A special gasometer which had been calibrated by the Ontario Department of Weights and Measures was used. A graph obtained accordingly for the relation between pressure difference and rate of hydrogen flow through the 0.1286 in. diameter orifice as plotted on a logarithmic scale is given by Fig. 13. The values given for rates of hydrogen flow are for a temperature of 60°F. and a pressure of 30 in. Hg.

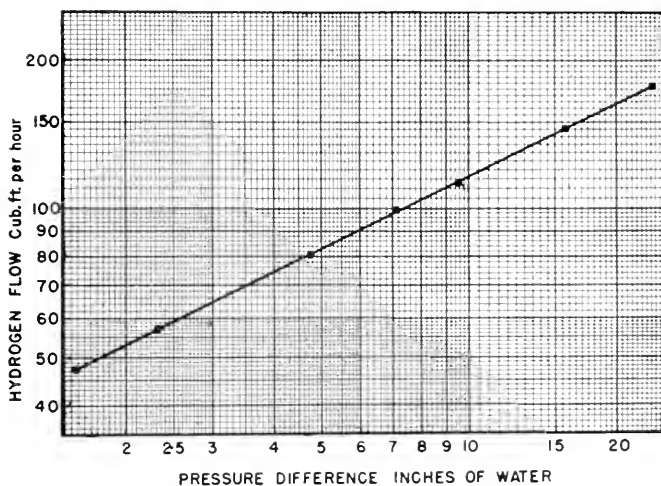


FIG. 13. Calibration graph for orifice 0.1286 in. diameter.

Accuracy of Measurement of Thermal Efficiency

The accuracy of measurement of I.H.P. by the motoring method, which is in general use, is not regarded as better than $\pm \frac{1}{2}$ of 1%. It is considered that the rate of hydrogen consumption was made with an accuracy of $\pm \frac{1}{4}$ of 1%. The values for I.T.E. given in this part are comparable with those obtained by Ricardo (16) and Burstall (2) when they used the motoring method of measuring I.H.P. Values for power and thermal efficiency are not given in more recent publications by others (1, 3).

The Spark Plugs

The spark plugs used for the experiments are illustrated by Fig. 14. Champion C.F.R.-8 is near the top of the commercial heat scale and was used as a

hot variety with a spark gap of 0.025 in. Spark plugs K.L.G. 100 and R2-S, rated at the bottom of a commercial heat scale, were used as cool varieties. The spark gaps of these plugs are not readily adjustable. They were used as supplied with gaps of 0.018 in. approximately. It would be expected according

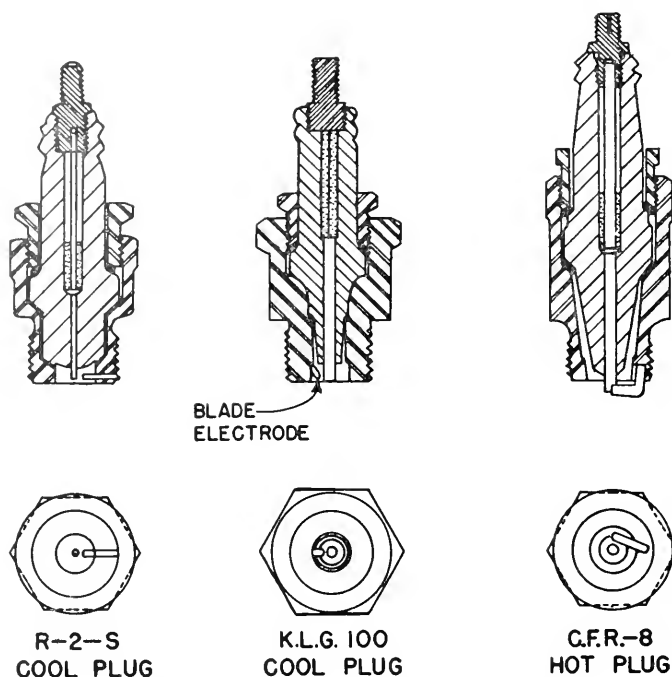


FIG. 14. Spark plugs used for the experiments.

to the designs that the K.L.G. plug would run hotter than the R2-S but it was shown by experiments, Section III, that neither attained the temperature required for the preignition of hydrogen-air mixtures in the conditions of the experiments of this Part.

Valve Timing

The low and high speed camshafts were designed to provide valve timings as tabulated below, according to the C.F.R. handbook. The given values were found to be correct within 1°.

	Low speed camshaft	High speed camshaft
Inlet valve opens	10° after t.d.c.	15° before t.d.c.
Inlet valve closes	34° after b.d.c.	50° after b.d.c.
Exhaust valve opens	40° before b.d.c.	50° before b.d.c.
Exhaust valve closes	15° after t.d.c.	15° after t.d.c.
Valve lift	0.238 in.	0.312 in.
Valve overlap	5°	30°

When the high speed camshaft was used, the exhaust valve with a lift of 0.312 in. was off its cooling seat for 155° of crank revolution. When the low

speed camshaft was used, the exhaust valve with a lift of 0.238 in. was off its cooling seat for 145° of crank revolution.

Exhaust Valves

The types of sodium cooled and uncooled silchrome exhaust valves used for the experiments described in this Part are illustrated by Fig. 15.

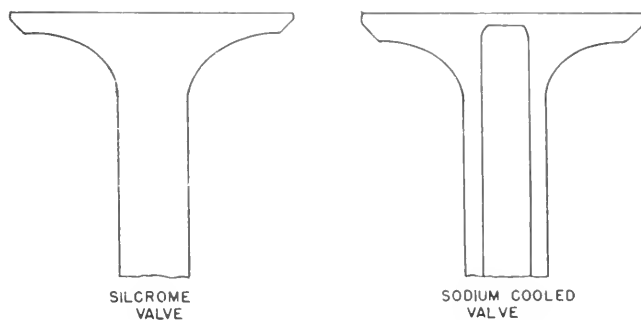


FIG. 15. Types of exhaust valves used for the experiments.

THE DECOMPOSITION, OXIDATION, IGNITION, AND
DETONATION OF FUEL VAPORS AND GASES

XXVIII. THE THERMAL DECOMPOSITION OF *n*-PENTANE AS AFFECTED
BY THE FLOW CONFIGURATION IN KING REACTOR NO. 10

BY H. SHANFIELD AND R. O. KING

THE DECOMPOSITION, OXIDATION, IGNITION, AND DETONATION OF FUEL VAPORS AND GASES

XXVIII. THE THERMAL DECOMPOSITION OF *n*-PENTANE AS AFFECTED BY THE FLOW CONFIGURATION IN KING REACTOR NO. 10¹

BY H. SHANFIELD² AND R. O. KING³

ABSTRACT

The thermal decomposition of *n*-pentane in a nitrogen atmosphere in the flow system of the King Reactor No. 10 has been investigated over the temperature range 647°C. to 727°C. The flow configuration in this reactor is such that an approach to the true reaction temperature can be obtained by successive increases in the rate of heat transfer. The apparent reaction order is unity, and the extrapolated energy of activation $34,000 \pm 2000$ calories per gram mole. Velocity constant data are fitted by the expression $\log_{10} k = 7.8 - (34,000/2.3 RT)$. The low activation energy may be due in part to catalysis by the Vycor surfaces. A Rice free-radical mechanism can account for the reaction products quantitatively and qualitatively. On this basis the relative chance of reaction of free radicals with primary and secondary hydrogens in the *n*-pentane molecule is 1:6 respectively.

INTRODUCTION

An investigation of reaction kinetics in flow systems is usually accompanied by some uncertainty in respect of the temperature of the reaction. Reactor No. 10, which incorporated a novel flow configuration, was first used for oxidation reactions, Part I (2). Its design is such that reaction temperature can be estimated with a fair degree of accuracy. *n*-Pentane was decomposed thermally in the reactor in order to obtain velocity constant data in a sparsely explored temperature region and an estimate of the activation energy of the reaction. The thermal decomposition of pentane was of interest because of the reactions that occur when mixtures with air are ignited by the heat of compression in an Otto cycle engine.

EXPERIMENTAL ARRANGEMENTS

A pentane-nitrogen mixture was used for the experiment. The rate of supply of nitrogen was always 300 cc./min. and *n*-pentane concentration was maintained at 0.0219 mole fraction, except when reaction order determinations were made. It was then varied from 0.0219 to 0.00365 mole fraction.

The reactor design is illustrated by Fig. 1. It will be seen that an inverted cup was formed in the end of a Vycor glass tube having an external diameter such that an annulus 1.0 mm. wide was formed between it and a concentric outer tube, also of Vycor. A transite washer fitted tightly in the outer tube formed the base of the reaction space. The washer was provided with a central opening through which the pentane-nitrogen mixture was admitted as a stream-

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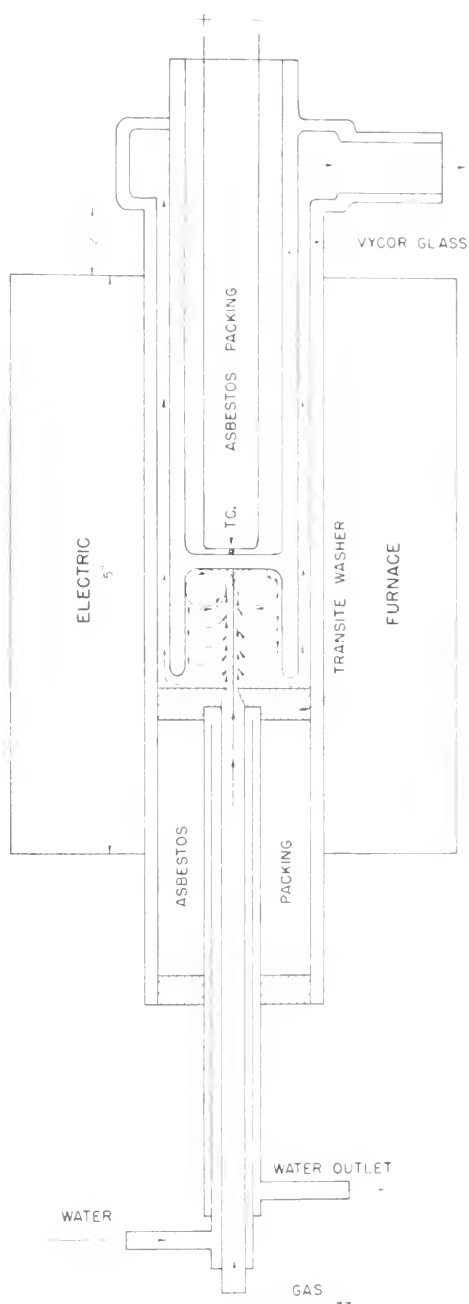


FIG. 1. King reactor No. 10.

line jet issuing from an orifice in the end of a water cooled inlet device. The jet impinged on the horizontal surface of the cup and produced a flow configuration which comprised a toroidal vortex in the *upper* end of the cup. It was expected therefore that reaction rate would not appreciably be affected by the transite washer which moreover attained a somewhat lower temperature because it did not provide complete thermal insulation between the upper and the cooler lower part of the reactor. Experiments were however carried out with a reactor constructed entirely of Vycor. The results of these were not different from those obtained when the transite washer was used and cleaning was difficult because the sole access to the reaction space was through the small hole provided for the orifice of the water cooled mixture inlet. Cleaning was accomplished easily when a removable transite washer was fitted in the reactor and this arrangement was used for all of the experiments described in this paper.

The reaction space included the volumes of the cup and of a length of the annular space. It was found by separate experiments that reaction occurred at an appreciable rate in a length of 6 cm. of the annular passage from the cup to the exit. The total volume of reaction space was estimated accordingly to be 5.6 cc. The time of residence of the mixture in the reaction space, if based on an average temperature of 750°C., was therefore 0.33 sec., approximately.

The kinetic energy supplied to the toroidal vortex by the jet of reacting mixture is absorbed mainly by surface friction; a factor which determines rate of heat transfer. In accordance with this view, the rate of heat transfer may be taken as proportional to the kinetic energy in the jet. Orifices 2.0, 1.0, 0.5, and 0.25 mm. in diameter were used for the experiment. The kinetic energy supplied accordingly to the toroidal vortex varied with the square of the velocity of the jet and this velocity varied inversely with the square of the diameter of the orifice. Thus when orifice diameter was reduced from 2.0 to 0.25 mm., and rate of mixture supply remained unchanged, the rate of supply of kinetic energy to the vortex increased 64-fold and the rate of heat transfer from the *surface in contact with the vortex* tended to increase in the same proportion.

Temperatures as measured by the thermocouple, Fig. 1, were taken as indicated reaction temperatures. They were varied over the range 650°C. to 750°C. When steady temperatures were established a sample of the effluent gas was bled off the system without a disturbance of the pressure. Decomposition data and product analyses were obtained accordingly at intervals of 10°C. when each of the four orifices were used. In addition, a limited series of experiments was made to determine heat transfer characteristics.

Fig. 2 is a schematic diagram of the over-all apparatus used. Cylinder nitrogen was passed through a purifying train to remove oxygen, carbon dioxide, and water. *n*-Pentane (99% purity) was delivered to the nitrogen at the required rate by means of a microdoser *M*, a device previously described (3). The mixture entered the electrically heated reactor where decomposition occurred. The reaction products were subsequently analyzed by fractional distillation in the LeRoy still (4), in conjunction with the Toepler pump and a constant volume burette. Hydrogen was determined by diffusion through a hot palladium tube. In addition, analyses were confirmed by mass spectrometer.

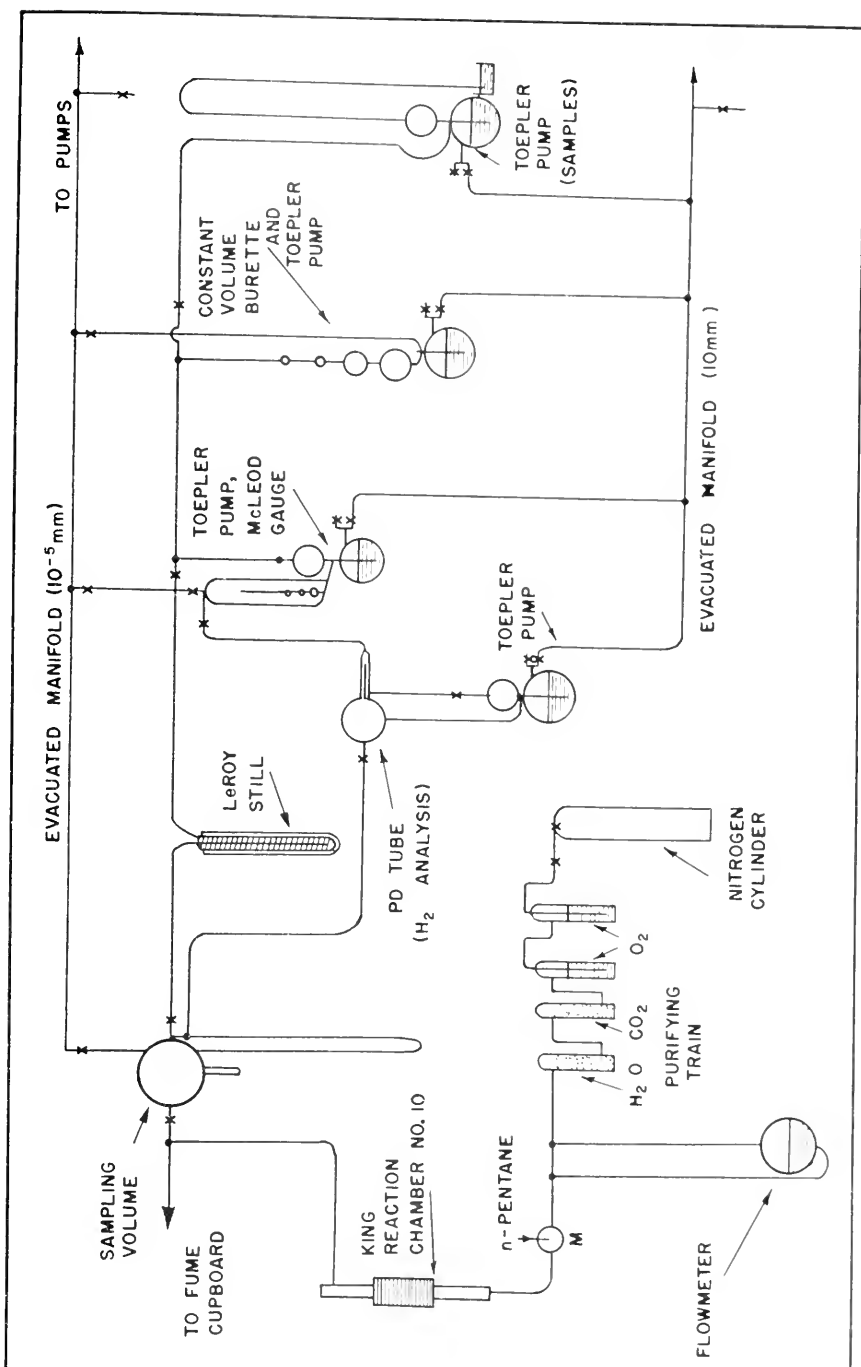


Fig. 2. Arrangement of apparatus.

RESULTS AND DISCUSSION

In Fig. 3 the percentage conversion of *n*-pentane to other products is plotted against inlet orifice diameter, for temperatures as indicated by the thermocouple, ranging from 650°C. to 750°C. When the temperature is maintained

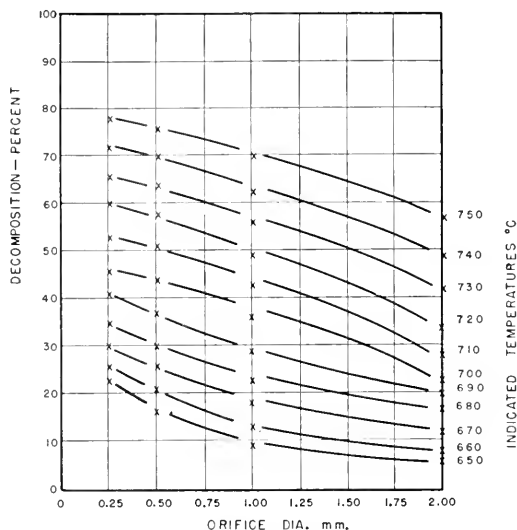


FIG. 3. Rate of decomposition at indicated temperatures ranging from 650°C. to 750°C. as related to orifice diameter.

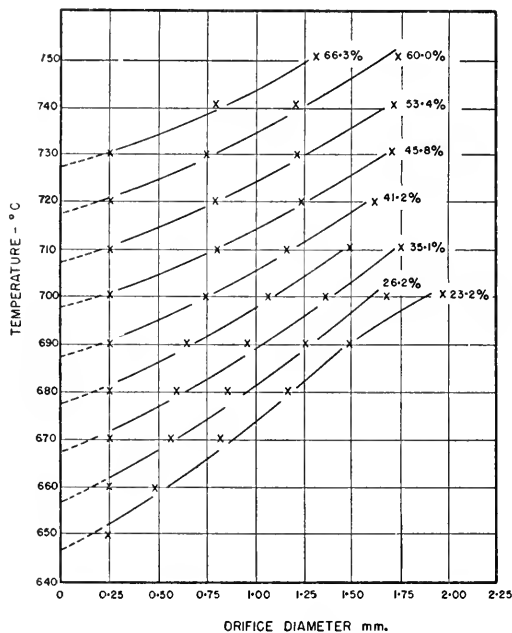


FIG. 4. Relationship between orifice diameter and the indicated temperature required for constant rates of decomposition ranging from 23% to 66%.

constant, decomposition decreases with increasing orifice size. These data are replotted in Fig. 4 for various constant degrees of conversion. This shows that the thermocouple temperature required to bring about a certain percentage decomposition decreases with decreasing orifice diameter. This effect appears to arise from the superior heat transfer rates obtained when the kinetic energy supplied to the vortex in the reactor increases with an increase in jet velocity. It is assumed that the temperatures to which these curves tend at zero diameter orifice are the true reaction temperatures.

Reaction temperatures could have been raised to the degree required for a higher rate of decomposition than the maximum of 78% attained when the indicated temperature was 750°C. and the mixture was admitted through the 0.25 mm. diameter orifice. This, however, would have produced a larger proportion of H_2 , CH_4 , and carbon in the products. The rate of carbon formation was negligible in the conditions used for these experiments, the carbon that was formed appearing only as a darkening of the cool end of the reactor, after long continued use.

Reaction velocity constants have been calculated from the decomposition data by the use of Benton's equation for reactions taking place at constant pressure in flow systems (1). Activation energies were estimated in the usual way from a plot of $\log_n k$ against $1/T$, T being absolute temperature in °K. Fig. 5 shows such a plot for the data resulting from extrapolation to zero diameter orifice. A straight line is obtained whose slope yields an energy of activation of 34,000 calories per gram mole for the reaction. Fig. 6 is a plot of the apparent activation energies calculated from the decomposition-temperature data for each orifice diameter, as well as the extrapolated value. The S-

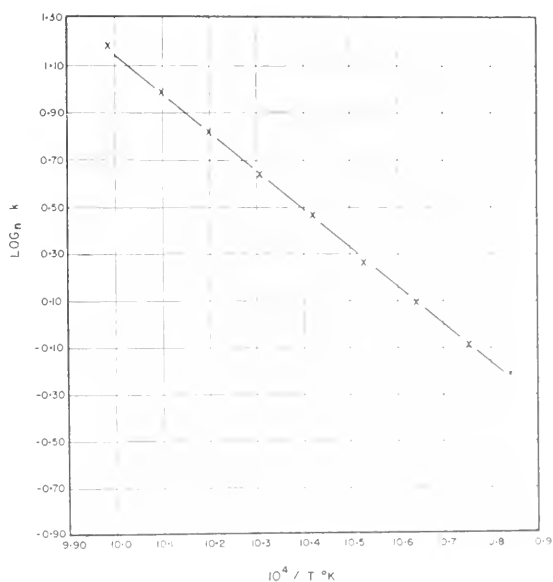


FIG. 5. Extrapolation to zero diameter orifice temperature range 647° to 727°C.

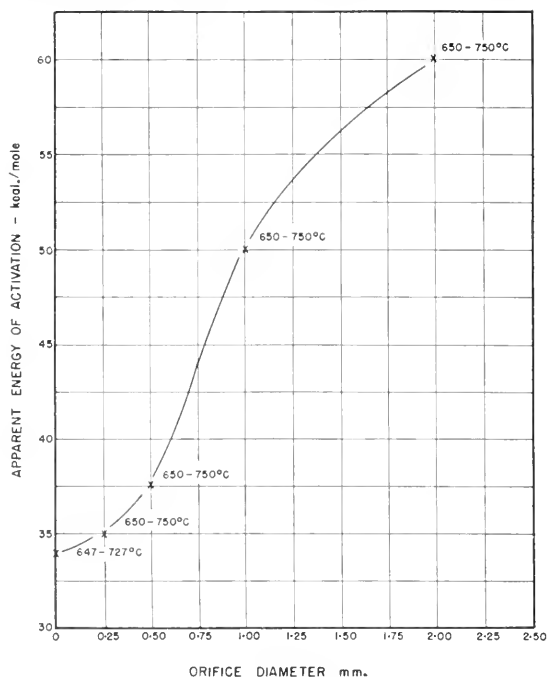


FIG. 6. Apparent energy of activation as related to orifice diameter, temperature ranges as shown.

shaped curve ranges from 60,000 to 34,000 calories per gram mole, from a relatively low rate of heat transfer case to the ideal one. The extremely low activation energy found in this work points to possible catalysis by the reactor surfaces. A preliminary experiment in which the reactor annulus was packed with Vycor fibers has shown a significant increase in reaction rate.

Flow methods are not generally used for studies of reaction kinetics and reactor No. 10 differs from the conventional type in that the flow configuration in it incorporates a toroidal vortex in addition to the laminar flow to be expected in a narrow annulus. In the light of results for oxidation reactions in reactor No. 10 given by King in Part II (2), unusual kinetic effects are to be expected because of the enhancement of heterogeneous reactions. Thus when the reactor is used for a study of decomposition reactions relatively low values for activation energy and the pre-exponential factor might well be expected.

Heat transfer data are plotted in Fig. 7. This figure is a plot of indicated temperature against orifice diameter for a constant electrical power input. The broken line, graph (3), shows the temperature condition when no gases pass through the reactor. When nitrogen alone is admitted at the usual flow rate, graph (2) is obtained. When pentane is added to the nitrogen, graph (1) is obtained. There is a successive drop in thermocouple temperature as orifice diameter is decreased, owing to increasing heat transfer rate, and the gas temperature approaches the indicated temperature. It appears reasonable to assume that extrapolation to zero diameter orifice would yield the true gas

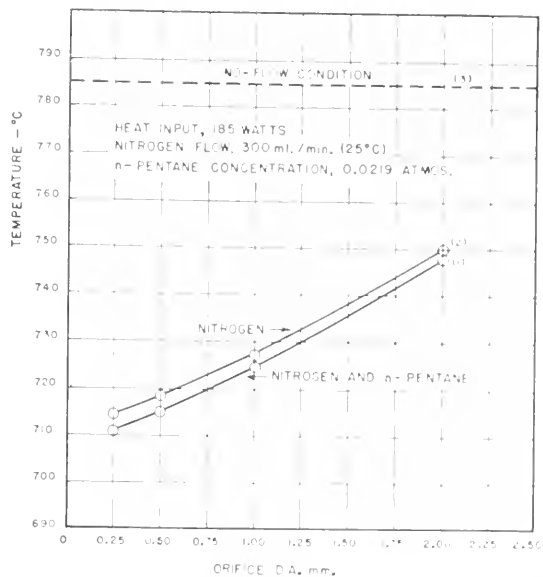


FIG. 7. Indicated temperature for a constant rate of heat input as affected by orifice diameter.

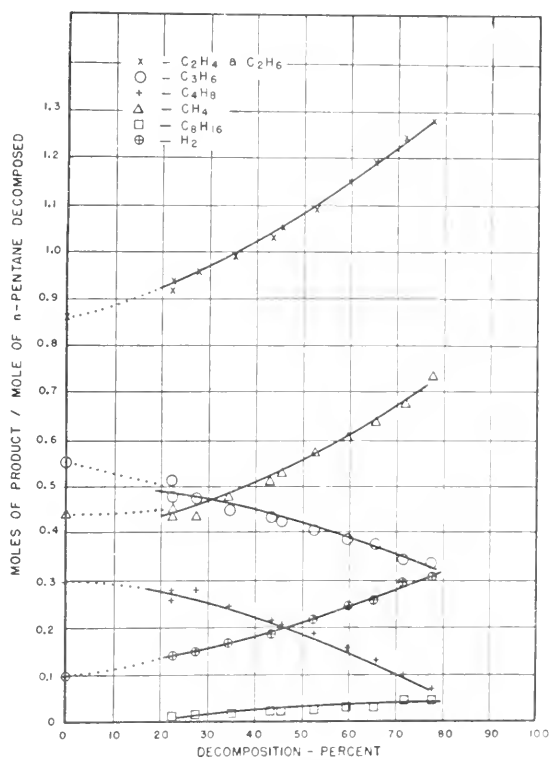


FIG. 8. Product selectivities as affected by the degree of decomposition.

temperature, and the results given by the graphs in Fig. 4 were obtained accordingly. The difference between graphs (2) and (1) is due to the endothermicity of the decomposition reaction.

REACTION MECHANISM

Analyses of reaction products are shown by the graphs of Fig. 8. Ethylene-ethane, propylene, butene-1, unreacted *n*-pentane, and the octenes were determined directly by fractional distillation. Methane was estimated by difference from the carbon-hydrogen balance. The absence of propane was confirmed by mass spectrometer analysis. In agreement with previous data, the moles of a particular product per mole of hydrocarbon decomposed i.e. the selectivity seems to depend upon the degree of decomposition rather than the temperature at which it was attained. It is for this reason that temperature does not appear as a variable on this figure.

The data are replotted on a different basis, Fig. 9. For this purpose the following mechanism is postulated:

- (1) $C_5H_{12} \rightarrow 2C_2H_4 + CH_4$
- (2) $C_5H_{12} \rightarrow C_2H_6 + C_3H_6$
- (3) $C_5H_{12} \rightarrow C_2H_4 + C_3H_6 + H_2$
- (4) $C_5H_{12} \rightarrow C_4H_8 + CH_4$
- (5) $C_2H_4 \rightarrow \frac{1}{4}C_8H_{16}$

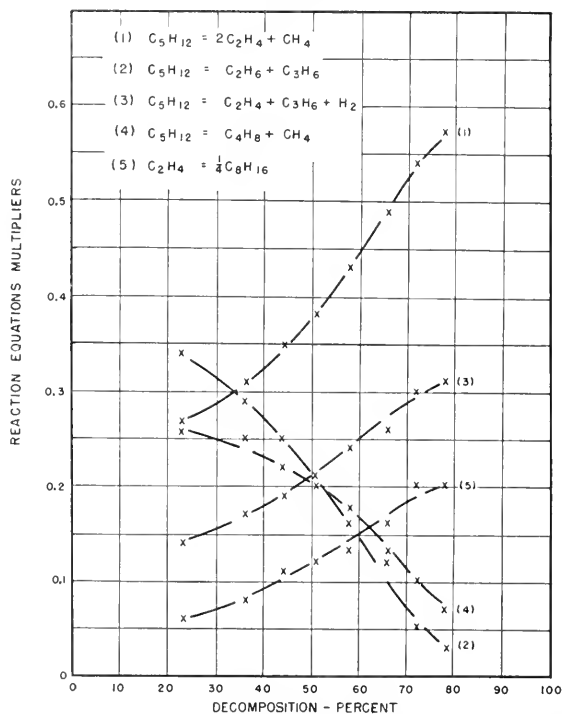
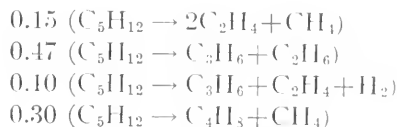


FIG. 9. Reaction equation multipliers as affected by per cent decomposition temperature range, 650° to 750°C.

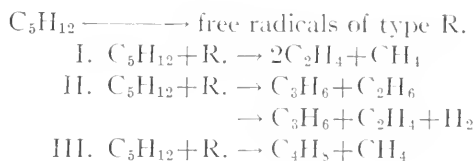
The ordinates of the figure represent multipliers which must be applied to these equations to fit the results; abscissae are per cent decomposition. When the data of both Figs. 8 and 9 are extrapolated to 0% decomposition, the following product composition is obtained:

Components	Moles /mole <i>n</i> -pentane decomposed
$C_2H_4 + C_2H_6$	0.87
C_3H_6	0.57
C_4H_8	0.30
H_2	0.10
CH_4	0.45 (by difference)
Total	2.29

Presumably these are the primary products of decomposition of *n*-pentane under these experimental conditions. Similarly the primary reaction equations are:



The Rice free-radical mechanism postulates the following series of reactions for the thermal decomposition of *n*-pentane:



Reaction I results from the free radical R. attacking the 1-position hydrogen, II by the attack of the 2-position secondary hydrogen, and III by attack of the 3-position secondary hydrogen. Rice assumed (5) that the chance of reaction of R. with primary and secondary hydrogens in the hydrocarbon molecule was 1:2 respectively. In the present work the chances of reaction of R. with 1, 2, and 3-position hydrogen atoms in the *n*-pentane molecule are:

$$\frac{0.15}{6} : \frac{0.47+0.10}{4} : \frac{0.30}{2} \text{ or } 1 : 5.7 : 6.$$

That is, the present work points to a ratio of 1:6 instead of 1:2. This high ratio may be related to some catalytic effect of the surface.

REACTION ORDER

The apparent reaction order was inferred from experiments in which the initial *n*-pentane concentration was varied. The results are shown in Fig. 10. The data show essentially no change in degree of conversion for a large change

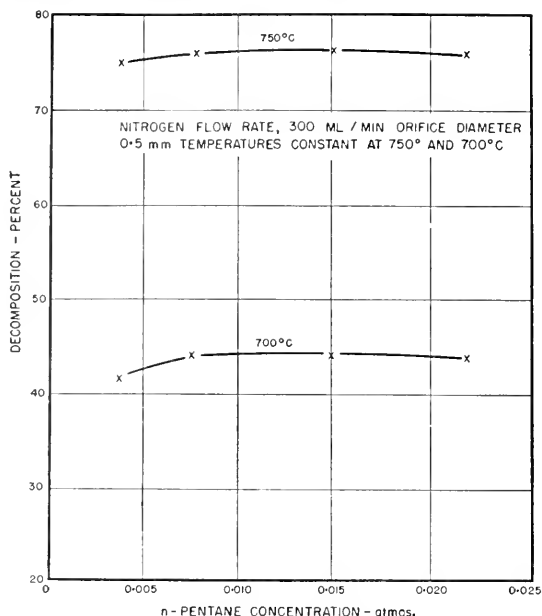


FIG. 10. Per cent decomposition as affected by reactant concentration.

in *n*-pentane concentration, which is one of the criteria of a first order reaction. This of course does not detract from the possibility that the reaction is catalytic.

ACKNOWLEDGMENT

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THE OXIDATION, DECOMPOSITION, IGNITION, AND
DETONATION OF FUEL VAPORS AND GASES

XXIX. THE ROLE OF NUCLEI IN THE IGNITION BY COMPRESSION OF
GASEOUS HEPTANE AIR MIXTURES: FIRST PAPER

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XXIX. THE ROLE OF NUCLEI IN THE IGNITION BY COMPRESSION OF GASEOUS HEPTANE-AIR MIXTURES: FIRST PAPER¹

BY R. O. KING² AND A. B. ALLAN³

ABSTRACT

The temperature of a special plug protruding into the combustion chamber of a C.F.R. carburetor engine was adjustable to provide a surface at temperatures higher, lower, or equal to that of the exhaust valve whether it was uncooled or sodium cooled. Compression ratio was always adjusted for maximum power output. This optimum value varied with the temperature of the exhaust valve as well as with mixture strength. These factors are dependent variables. The experimental results support the view that mixtures richer than 25% weak were ignited by nuclei of finely divided carbon derived from pyrolysis of the heptane and that the inflammability of the nuclei increased over the mixture range 25% to 40% weak owing to their absorption of aldehydes. The rate of formation of aldehydes increased as mixture strength was further reduced and it appears that nuclei of ignition then became resinous substances, formed of the condensation products. Further experiments with weak mixtures are to be described in a second paper on the subject of this Part.

INTRODUCTION

Hydrogen in mixtures with air was used as the fuel for experiments with a C.F.R. engine described in Part XXVII (7) and ignition by compression did not occur even at values of compression ratio rising to 12:1 unless nuclei of finely divided carbon were provided by the decomposition of lubricating oil vapor.

Paraffin fuels differ from hydrogen in that they provide nuclei of ignition at values of the compression ratio which, if speed is constant, depend mainly on the factors of mixture strength and the temperature attained by the exhaust valve. Experiments carried out with the C.F.R. engine in the conditions required to determine the effect of these factors are described in this Part. The fuel used was heptane as supplied by Phillips Petroleum Company for the ASTM method of knock rating. Operating conditions were as adopted for the experiments with acetaldehyde and diethyl ether Part XX (2), and the subsequent experiments with heptane, hexane, and pentane, Part XXI (6) and Part XXIV (3), namely: engine speed 400 r.p.m., air supply temperature 50° F.; engine coolant water 100° F. at the outlet from the cylinder head jacket and approximately 97° F. at the entrance to the jacket of the cylinder barrel; a subnormal charge density, 64% of normal was used.

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I. EXPERIMENTAL ARRANGEMENTS

The standard shrouded inlet valve of the engine was replaced by an exhaust valve in order to eliminate a swirl in the mixture entering the cylinder. The engine was direct connected to a d-c. generator arranged as a swinging field dynamometer. Speed was maintained at 400 r.p.m. by adjustment of load.

The air supply was refrigerated to remove excess moisture in order to avoid ice formation in the carburetor. The temperature of the air was then raised to 50° F. prior to its supply to the carburetor. Engine cooling was by a thermostatically controlled water circulation.

The subnormal charge density was used in order to enable the engine to tolerate the degree of detonation caused by the compression ignition of mixtures richer than 25% weak. It was obtained by fitting a choke tube to the standard C.F.R. carburetor, as described in Part XIX (5, pp. 31 and 40). The choke tube required for a reduction of charge density to 61% of normal was $\frac{1}{4}$ in. only in inside diameter because of the low engine speed of 400 r.p.m. The pressure in the choke tube during the induction stroke was found by a separate experiment to be approximately half an atmosphere. Vaporization of the fuel was promoted accordingly and further by the heat of compression, by that of the residual gas, and by heat absorbed from hot surfaces in the combustion chamber.

Abbreviations used in subsequent text are: C.R. for compression ratio, M.S. for mixture strength, I.T.E. for indicated thermal efficiency, and t.d.c. for top dead center. Stoichiometric mixtures are described as "correct" in the text and as C.C.M. on graphs. Mixture strength is described as per cent weak or rich according to the percentage by which the concentration of fuel in the mixture with air is less or more than is required for a correct mixture.

II. METHOD OF EXPERIMENT

The method was based on the use of the "temperature plug" illustrated by Fig. 1. This device will be described as a "T.P.". It was of mild steel machined from solid stock and contained an air cooling device and the leads to a thermocouple for the measurement of the temperature of the rounded end, which protruded slightly into the combustion chamber. The temperature attained by that end when not cooled was from 300° to 400° F. higher than that of the exhaust valve, depending on the variation of heat load with mixture strength. Cooling air was supplied from a high pressure source and provision was made for regulation of the flow in a manner to maintain the temperature of the rounded end at any particular value lower than that attained when it was not cooled.

The C.R. required for ignition was always adjusted to the value at which maximum combustion pressure occurred at the time necessary for the development of maximum power output. This time, taken in degrees of crank angle, varied little from 10° after t.d.c. The corresponding C.R. is the optimum value and is described in subsequent text as the Opt. C.R. Thus the end of the "delay period" required for nuclear ignition was fixed and consequently the

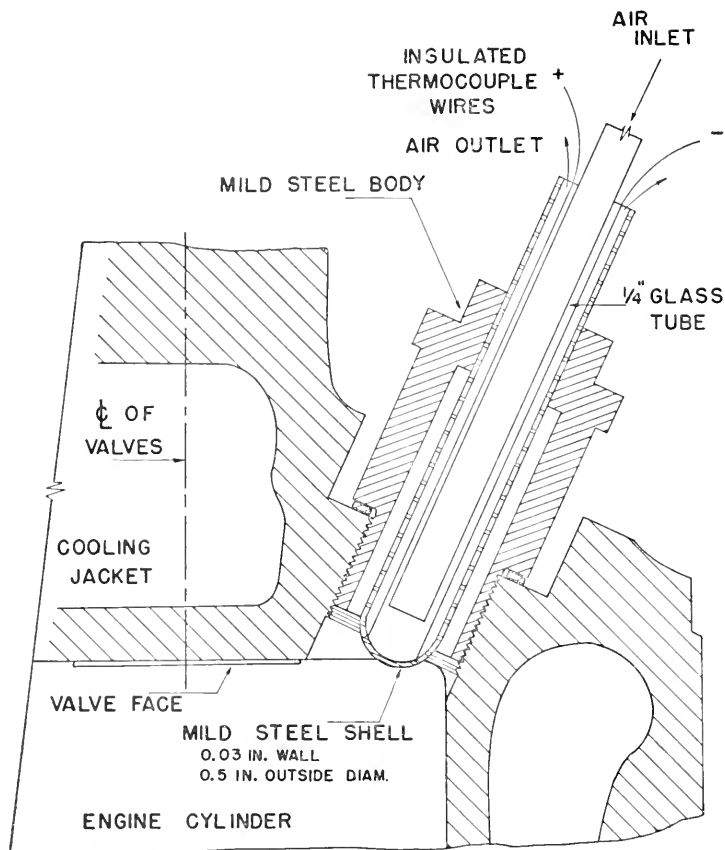


FIG. 1. Illustration of the air-cooled temperature plug as fitted in place of the bouncing pin.

values obtained for I.H.P. and I.T.E. were always consistent with particular values of M.S.

Preliminary Experiments

These were carried out in order to illustrate by indicator diagrams the method of using the T.P. Heptane was used as the fuel and the mixture with air was adjusted to be nearly correct; as measured it was 2.3% weak. Pressure-time and rate of pressure change diagrams were taken simultaneously by a Dumont dual beam oscilloscope. The cylinder was provided with three spark plug holes in the wall. One was used for a "Sunbury" magnetic flux pressure pickup to obtain rate of pressure change diagrams. A "Photocon" capacitance type pickup was used in another hole to obtain pressure-time diagrams. The third hole was fitted with a mild steel blank plug. Timing blips were fed into the electronic circuit at t.d.c. and at 10° intervals before and after. The blips

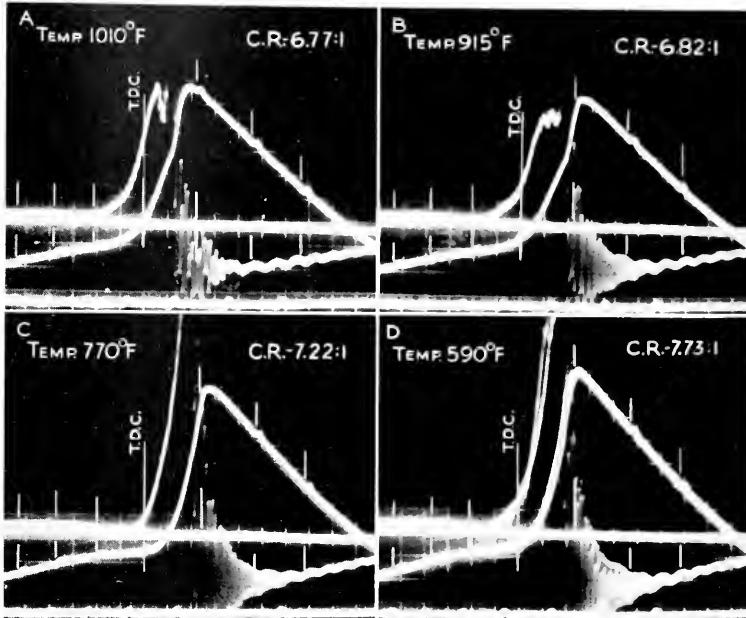


FIG. 2. Pressure-time and rate of pressure change diagrams taken simultaneously to show the increase in the Opt. C.R. at which ignition occurs as plug temperature is reduced to be equal to or less than that of the exhaust valve, nearly correct heptane-air mixtures.



are not always plainly visible on the photographic copies of the diagrams and short vertical lines have been added to mark their positions.

Four of the double diagrams taken during the experiments are reproduced as Fig. 2 and numbered A to D.

A Diagrams

These were taken with the T.P. uncooled. It then attained a temperature of 1010°F . and the Opt. C.R. was 6.77. It is shown by the pressure-time diagram that maximum combustion pressure occurred at 8° after t.d.c. and it is evident from the initially low rate of pressure rise that combustion was initiated by surface ignition. However, before it was completed by the normal thermal process of flame propagation, nuclear ignition accompanied by detonation occurred in the mixture ahead of the flame front (the end gas) and combustion was completed in 2° of crank revolution. Thus detonation was a consequence of nuclear ignition of the end gas.

B Diagrams

The T.P. was cooled to 915°F . A small increase of C.R. to 6.82 only was then required in order to obtain the optimum value. The characteristics of combustion were as described in respect of the A diagrams. The occurrence of both maximum combustion pressure and nuclear ignition about 1° of crank revolution later than shown by the No. 1 diagrams is without significance because it represents the variation that may occur in successive cycles.

C Diagrams

The T.P. was cooled to 770°F . and the Opt.C.R. then became 7.22. Both diagrams show that the T.P. ceased to initiate surface ignition when its temperature had been reduced to 770°F . The rate of heat liberation by the oxidation reaction proceeding on its surface was then too low to raise the adjacent mixture to the temperature required for an igniting effect. The ignition that did occur is attributed to the nuclei formed during compression. The absorption of heat by the decomposition reaction accounts in part for the failure of compression pressure to rise in the normal manner during the latter part of the compression stroke, as is shown by the rate of pressure change diagram.

D Diagrams

The T.P. was cooled to 590°F . and a relatively large increase in C.R. to 7.73 was then required for an optimum value. The diagrams differ from the C pair in showing that an increased rate of combustion followed the initiation of nuclear ignition at the higher value of Opt.C.R. The temperature of the plug appears to have been reduced to be lower than that of the exhaust valve because Opt.C.R. remained constant as plug temperature was further reduced to 520°F . and then to 420°F . if mixture strength were maintained constant as shown by diagrams not reproduced.

Mechanical and Gas Vibrations

Low frequency vibrations which appear in the expansion stroke and extend into the high frequency gas vibrations set up by nuclear ignition are mechanical vibrations of the engine. They were reproduced by holding a small vibrating engraving tool in contact with the outer end of the pressure pickup. The high frequency gas vibrations shown by the A diagrams are confused because pressure rise due to surface ignition began 10° before t.d.c. A single set of high frequency pressure vibrations appears on the B diagrams when plug temperature was reduced by nearly 100° F. and there was a consequent delay in the occurrence of surface ignition. A double set of high frequency pressure waves appear on the D diagrams because they include parts of two cycles which differed slightly in timing.

Exhaust Valve Temperature and Opt.C.R. as Affected by Mixture Strength

An experiment with a particular mixture strength was begun with the T.P. uncooled and values were obtained for its temperature and the corresponding Opt.C.R. The T.P. was then cooled to successively lower temperatures and corresponding values for Opt.C.R. determined as described at the beginning of this section. The experiment was continued until a constant value for Opt.C.R. was obtained for successively lower plug temperatures. It was indicated accordingly that the plug temperature had become equal to and then lower than that of the exhaust valve. The temperature of equality could then be determined from a graph for the relation between plug temperature and Opt.C.R. provided great care had been taken to maintain constancy of operating conditions.

Examples of the graphs obtained when mixtures were 7.7% weak, 24% weak, and chemically correct are given by Fig. 3. Graphs obtained when mixtures were 10%, 20%, 56%, and 102.5% rich are given by Fig. 4. It will

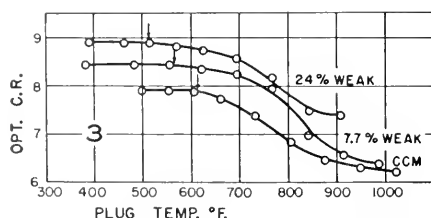


FIG. 3. Graphs for the relation between Opt. C.R. and plug temperature, heptane-air mixtures correct and weaker. The temperature at which that of the plug was the same as the temperature of the exhaust valve is indicated by small arrows.

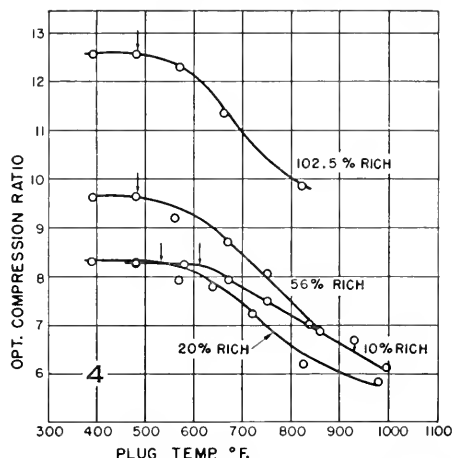


FIG. 4. Graphs for the relation between Opt. C.R. and plug temperature for rich heptane-air mixtures. The temperature at which that of the plug was the same as the temperature of the exhaust valve is indicated by small arrows.

be seen by reference to the graphs that the temperature at which the T.P. ceases to affect the value of Opt.C.R., by becoming equal to that of the exhaust valve, is shown with a fair degree of accuracy by the small arrows on the graphs.

It is of interest that Opt.C.R. tended to become dependent on M.S. only, as that factor was increased to be greater than 20% rich. Thus the temperature of the exhaust valve was 530° F. for a mixture 20% rich. It diminished only to 480° F. for a mixture 56% rich and remained at that temperature as M.S. was increased to be 102% rich.

The Relation between Opt.C.R. and Plug Temperature for Heptane-Air Mixtures Leaner than 37½% Weak

The measurement of exhaust valve temperature by the T.P. method is based on a variation of Opt.C.R. with plug temperature when M.S. has particular values, as illustrated by the graphs of Figs. 3 and 4. When however the values of M.S. were less than 37½% weak, a nearly constant value of Opt.C.R. was obtained for a particular value of mixture strength while the temperature of the plug was varied over a wide range. Experimental results obtained for particular values of M.S. ranging from 10.5% weak to 72% weak are given by the graphs of Fig. 5. They afford an explanation for the failure of the T.P.

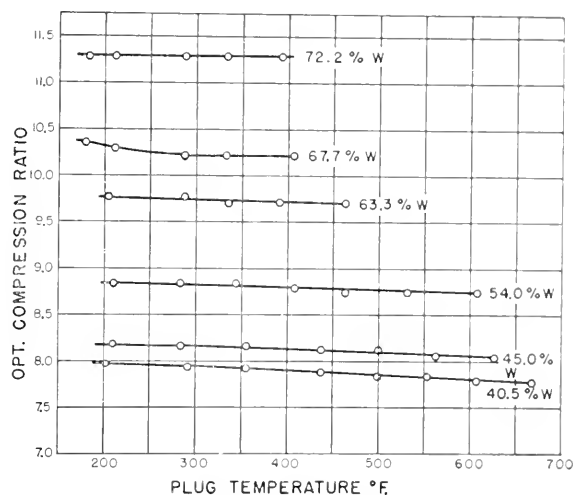


FIG. 5. Graphs showing that the relation between Opt. C.R. and plug temperature remains nearly constant at particular values of mixture strength ranging from 40.5% weak to 72% weak.

method to measure the temperature of the exhaust valve when mixtures were leaner than 37½% weak. The experimental results are of even more interest in showing that for any particular mixture within the range 40.5% weak or weaker, Opt.C.R. remains substantially constant while plug temperature is increased from 200° F. to higher temperatures ranging from 400° F. for a mixture 72% weak to 675° F. for a mixture 40.5% weak. If the plug temperature remained constant at 400° F., Opt.C.R. would vary with M.S. only over the range 40.5% weak to 72% weak.

III. EXPERIMENTAL RESULTS OBTAINED WHEN THE C.F.R. ENGINE WAS OPERATED WITH IGNITION BY COMPRESSION

Compression ignition experiments described in this Section were carried out over a wide range of heptane-air mixtures, while the temperature of the exhaust valve was measured by the T.P. method and then by a direct thermocouple method. Further experiments were then carried out with the T.P. method used to measure the temperature attained by a sodium cooled exhaust valve. C.R. was always adjusted to an optimum value and corresponding values for I.H.P. and I.T.E. were determined.

Exhaust Valve Temperature Measured by the T.P. Method; Heptane-Air Mixtures

The solid C.F.R. exhaust valve used for the experiments, and for those described earlier, was of nichrome steel with a stellite seating. The heptane-air mixtures ranged from 70% weak to 90% rich. The experimental results are given by the graphs of Fig. 6. Significant features are as follows:

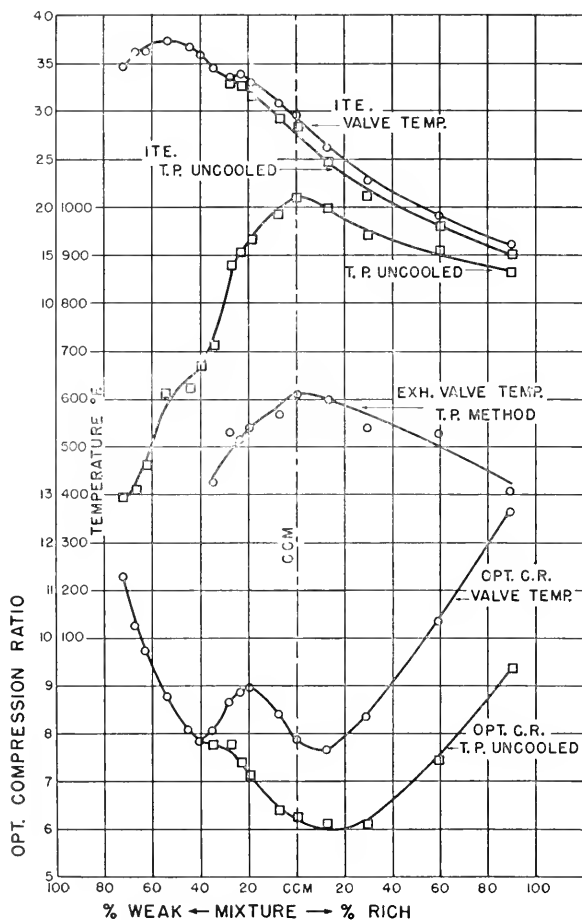


FIG. 6. Graphs for experimental results obtained when the temperature of the standard C.F.R. exhaust valve was determined by the temperature plug method, heptane-air mixtures.

When a correct mixture was used, the uncooled T.P. attained a temperature of 1020°F. , the corresponding values for Opt.C.R. and I.T.E. being 6.2 and 27.5% respectively. The temperature of the exhaust valve at the same mixture strength was found to be 610°F. by the indirect T.P. method; the corresponding values for Opt.C.R. and I.T.E. being 7.9 and 29% respectively. The exhaust valve temperature decreased to 440°F. as M.S. was increased from correct to 90% rich, while corresponding values for Opt.C.R. increased to 12.6.

The characteristics of the compression ignition of weak mixtures differed in a striking manner from those for rich mixtures. Thus as M.S. was decreased from the correct value, the temperature of the uncooled T.P. and that of the exhaust valve diminished rapidly and the corresponding value of Opt.C.R. increased in a normal manner until M.S. was 20% weak. Significant events then occurred as M.S. was further reduced to 10% weak. Thus the value for Opt.C.R. diminished from 9.0 to 7.8 instead of increasing, and I.T.E. tended to remain constant at $33\frac{1}{3}\%$. The leanest mixture for which the exhaust valve temperature could be determined was $37\frac{1}{2}\%$ weak and identical values were obtained for Opt.C.R. and I.T.E. when the temperature of the plug was 700°F. and that of the exhaust valve 420°F. The values of Opt.C.R. increased in a normal manner as M.S. was further reduced and the corresponding values for I.T.E. increased to a maximum of $37\frac{1}{2}\%$ when the mixture became 55% weak, although Opt.C.R. had increased to 8.8 only. The experiment was continued until M.S. was reduced to 72% weak. The I.T.E. had then fallen to 35% and Opt.C.R. had risen to 11.3. The relatively low value of $37\frac{1}{2}\%$ for maximum I.T.E. was shown by experiments described in Part XXIV (3, p. 240) to be due to the excessive proportion of the heat of the compressed mixture that is lost to the combustion chamber wall when extremely weak mixtures are used at a subnormal charge density in the conditions of the experiments.

Exhaust Valve Temperature Measured by Thermocouple; Heptane-Air Mixtures

The drilling of a small hole through the $\frac{3}{8}$ in. diameter stem of the C.F.R. nichrome steel exhaust valve in order to provide for thermocouple wires leading to a junction in the valve face was not attempted. The exhaust valve used for the experiments was therefore lathe turned from a bar of cold rolled mild steel. It was a replica of the standard C.F.R. valve except that the stem was made the same diameter as that of the C.F.R. sodium cooled valve, namely $\frac{7}{16}$ in. A hole $\frac{1}{8}$ in. diameter was drilled through the stem nearly to the valve face and then reduced to $\frac{1}{16}$ in. diameter. The $\frac{1}{8}$ in. hole was large enough to take iron and constantin wires insulated with fiber glass. The junction was brazed into the $\frac{1}{16}$ in. hole to be flush with the face of the valve. The end of the rocker arm which operates the valve was altered to provide a fork through which the thermocouple wires were carried to the temperature indicator. The mild steel valve has been used frequently for more than a year in the low heat load conditions of the experiments without showing any sign of deterioration even on the seating.

The T.P. was replaced by a blank steel plug and the experimental results then obtained are given by the graphs of Fig. 7. It will be noted that a graph

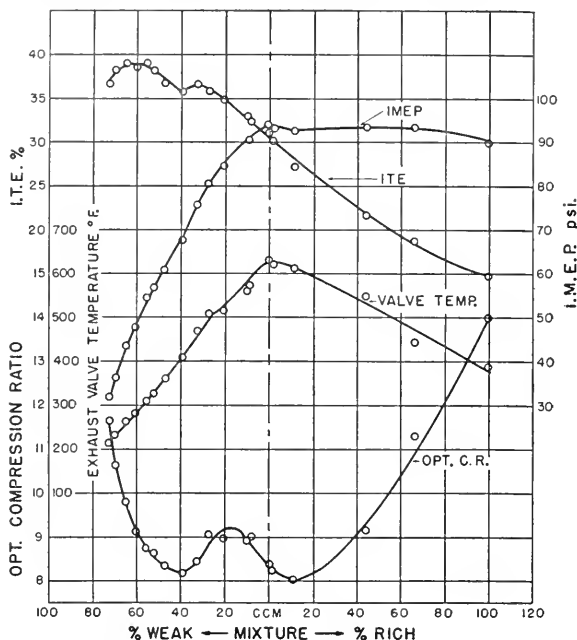


FIG. 7. Graphs for experimental results obtained when the temperature of a mild steel exhaust valve was measured by a thermocouple, heptane-air mixture.

for values obtained for I.M.E.P. is given. Similar I.M.E.P. values were obtained when the T.P. was used but were not shown on Fig. 6, in order to avoid confusion. It will be seen that the relation between Opt.C.R. and I.T.E. was the same as that obtained when the T.P. was used, see Fig. 6, within the limits of experimental error. The graphs for the relation between Opt.C.R. and M.S., Figs. 6 and 7, illustrate the effect of the increase in mixture temperature caused by the extra area of heated surface introduced into the combustion chamber by the T.P. Thus over the mixture range 44% weak to 25% rich, the Opt.C.R. required when the T.P. was used was from 0.1 C.R. to 0.3 C.R. lower than when the exhaust valve temperature was measured by the thermocouple.

The exhaust valve temperatures obtained by the two methods are plotted on a base of mixture strength (Fig. 8). It will be seen that the values fall closely on a single graph. The inconsistencies shown for values of M.S. exceeding 10% rich are not greater than would be expected in view of the irregularity of combustion that occurs in the operation of an engine by compression ignition in the circumstances. The irregularity may be due in part to incomplete vaporization of heptane in rich mixtures with air.

The Temperature of a Sodium Cooled Exhaust Valve as Measured by the T.P. Method; Heptane-Air Mixtures

The direct measurement of the temperature of a sodium cooled exhaust valve involves difficult experimental technique. It is a simple matter when the indirect T.P. method can be used. Temperature measurements were made

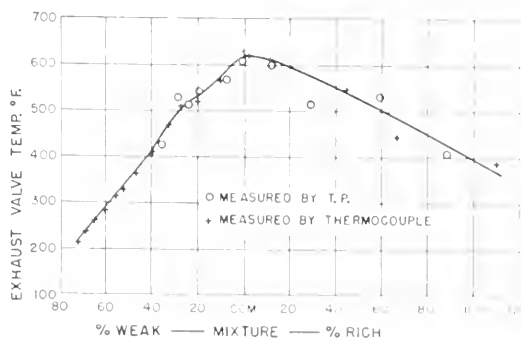


FIG. 8. Graph for a comparison of exhaust valve temperature as measured by the direct and indirect methods.

accordingly when a sodium cooled exhaust valve was fitted in the C.F.R. engine. The valve was of the type in which the hole drilled through the over-size stem extends into the head nearly to the crown. This type was used for hydrogen engine experiments and its design is illustrated by Fig. 15 of Part XXVII (7).

The results of experiments carried out with heptane-air mixtures ranging from 72% weak to 90% rich are given by the graphs of Fig. 9, which include a broken line graph for the temperature of the standard C.F.R. exhaust valve taken from Fig. 6.

It will be seen by reference to the relevant graphs that the temperature attained by the sodium cooled valve was the lower by 290° F. when the mixture was correct. Its temperature diminished more slowly than that of the solid valve as M.S. was increased and Opt.C.R. raised as required. This is attributed to the sodium cooling remaining effective, because I.M.E.P. and the consequent heat load remained nearly constant as shown earlier by Fig. 7.

I.M.E.P. and heat load decreased rapidly as M.S. was reduced from correct, with the result that the length of valve stem enclosed by the guide approached the temperature of solidification of the sodium and the rate of heat transfer from the head of the valve to the relatively cool guide was reduced. Thus the temperature of the sodium cooled valve was 100° F. only lower than that of the solid valve when mixtures ranged from 30% weak to the 10% weak at which the T.P. method of measurement became ineffective. Nevertheless the sodium cooled valve would continue to attain the lower temperature when still weaker mixtures were used even if the sodium solidified, because of its larger stem diameter.

The most significant effect shown to be due to a change from the solid to the sodium cooled valve was the consequent change in the combination of mixture strength and Opt.C.R. required for the initiation of nuclear ignition, as shown by the graphs of Fig. 9, which include a broken line graph for the temperatures attained by the C.F.R. standard solid exhaust valve. It will be seen that higher values for Opt.C.R. were required for mixtures ranging from 40% weak to 50% rich when the valve was sodium cooled. The maximum

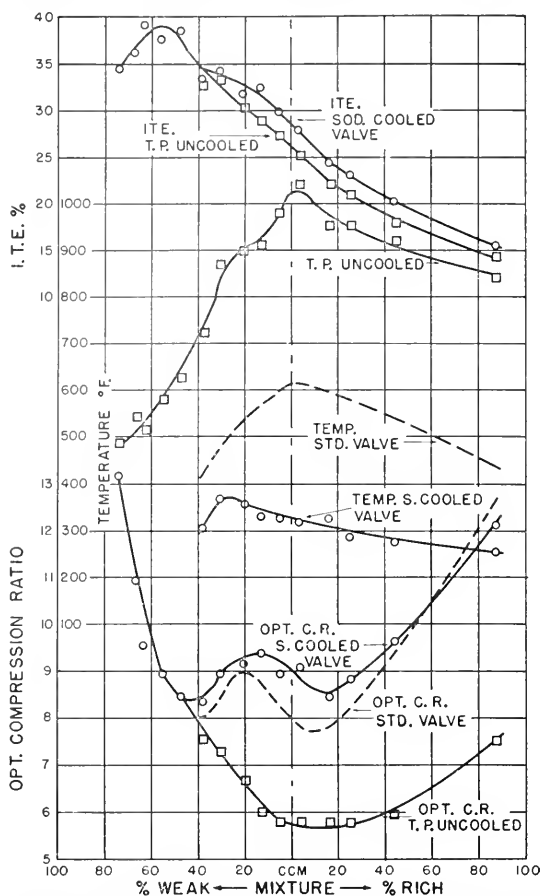


FIG. 9. Graphs for experimental results obtained when the temperature of a sodium cooled exhaust valve was determined by the temperature plug method, heptane-air mixtures.

difference occurred when the mixture was correct. Opt.C.R. was then 7.9 when the solid valve was used and 9.0 after a change was made to the sodium cooled valve.

The value of 28% was obtained for I.T.E. when the solid exhaust valve was used and the Opt.C.R. was 7.9 (see Fig. 6). When a change was made to the sodium cooled valve I.T.E. decreased to 27% although Opt.C.R. was higher at 9.0. The reduction of exhaust valve temperature by 290° F. at correct mixture, caused by sodium cooling, would be accompanied by a reduction in the temperature of the mixture at the end of compression. The observed increase in Opt.C.R. to 9.0 is regarded as having been required for the formation of an igniting concentration of nuclei in the cooler mixture.

IV. FLAME COLOR, LUBRICATING OIL EFFECT, KNOCK INTENSITY, COLD STARTING

Flame Color

A short length of polished Pyrex rod was used as a window. It was set in a mild steel mounting adapted to replace an 18 mm. spark plug in the cylinder

wall. The inner end of the Pyrex rod was set $\frac{3}{8}$ in. back from the cylinder wall and consequently tended to remain clean. Flame color was observed as mixture strength was increased from 75% weak to 100% rich. Compression ratio was always adjusted to the value required for maximum power output.

Mixture 75% to 40% Weak

The color was a brilliant light blue which became tinged with purple as M.S. was increased. The light intensity, as measured by a photomultiplier, was feeble.

Mixture 41% to 39% Weak

In this narrow range the purple tinge of the blue flame was replaced by white with a consequent marked increase in light intensity.

Mixture 39% Weak to 35% Rich

The flame was a brilliant white with an occasional tinge of yellow. Light intensity was so great that visual observations of the flame were necessarily brief.

Mixture 25% to 100% Rich

The brilliant white tended to pink as M.S. was increased to 30% rich. The color then changed to a bright orange as M.S. was further increased to 35% rich. The orange color persisted as M.S. was increased to be 100% rich. Light intensity diminished as color changed from white to pink and then to orange.

Effect of the Combustion of Lubricating Oil

It was shown by the hydrogen engine experiments described in Part XXVII (7) that the decomposition of lubricating oil *vapor* provided carbon nuclei which ignited the mixture with air before completion of the compression stroke. These experiments were carried out at engine speeds rising to 1800 r.p.m. and with normal charge density. Even so, an igniting effect arising from the lubricating oil did not occur until C.R. was raised to 12:1 and the rate of oil passing the piston increased because the top piston ring overlapped the three spark plug holes in the cylinder wall. Enough oil was then vaporized for the production of an igniting concentration of carbon nuclei.

The reactions required for the provision of nuclei of ignition by the vapor of lubricating oil would not be expected in the conditions of low heat load used for the experiments of this Part, and no evidence of such an effect was discerned. Lubricating oil passing the piston was necessarily burnt, at least in part, during combustion of the heptane, especially when air was in excess of that required for a correct mixture. Thus the flame color of heptane-air mixtures leaner than 41% weak was fundamentally a bright blue. The bright flashes of flame ranging in color from orange to white that were then observed appeared to be directly in front of the viewing window, not in the body of the mixture. They were attributed to combustion of the spray of oil thrown up from the periphery of the piston as its direction of motion reversed at t.d.c. It is possible that these bright flashes persisted as mixture strength was increased but were obscured by the intense white light emitted by the burning

carbon nuclei regarded as being responsible for the detonation of heptane-air mixtures richer than approximately 25% weak.

Combustion Knock

The combustion of mixtures leaner than 40% weak that occurred after nuclear ignition was notably silent. As the mixture was enriched, combustion knock increased slowly in intensity until the mixture was 25% weak. Intensity then increased rapidly to become severe at correct mixture. Little change in intensity occurred as M.S. was increased to be 80% rich. Knock intensity diminished slowly as M.S. was further increased.

Cold Starting

A mixture leaner than 40% weak was always used for cold starting. Ignition occurred immediately on raising C.R. to from one to two units higher than the optimum value used for continuous running. The C.R. was then lowered as the engine warmed up and adjusted to the value required for maximum power output for the measured mixture strength.

DISCUSSION

It is of interest to compare the experimental results of this Part with those obtained by others when combustible gaseous mixtures were ignited by rapid compression in a single stroke compression ignition machine and ignition temperature calculated according to the familiar equation,

$$[1] \quad T_1/T_0 = (P_1/P_0)^{1-1/\gamma} = (V_0/V_1)^{\gamma-1}.$$

Tizard in a paper on the causes of detonation in the end gas in a spark ignition engine (11) described experiments with heptane-air mixtures as carried out with a single stroke compression ignition machine made by Ricardo. The design of the machine is illustrated in the reference quoted. Both the volume and pressure ratios were observed. Thus an apparent value for γ was calculated from the second and third terms of equation [1], which allowed for loss of heat to the cylinder wall during compression and for the concentration of heptane vapor in the mixture with air. The value of γ calculated for a correct mixture was 1.31. It increased to 1.33 for a fuel to air ratio of 0.027 and decreased to 1.22 for a fuel to air ratio of 3.75. These apparent values for γ were obtained when the "delay period" preceding detonation was not maintained at a fixed value. The ignition temperature calculated accordingly varied $\pm 8^\circ \text{C}$. only, from an average value of 291°C . (555°F .). The delay period was taken as the time interval between the completion of compression and the sharp pressure rise caused by detonation. It is probable that if the compression ratios at which ignition occurred had been as required for a constant delay period, the calculated ignition temperature would have had even a more nearly constant value, over the M.S. range of the experiments.

The Effect of Surface Temperature on the Compression Ratio Required for Ignition

It was found by Tizard that the compression ignition temperature of heptane-air mixtures was nearly constant irrespective of the concentration of

heptane but that the C.R. ratio required for the igniting effect varied with the concentration and the delay period. When, however, ignition is by compression in an engine, the temperatures attained by surfaces in the combustion chamber have an important influence on the compression ratio required for the initiation of an igniting effect. The relation between surface temperatures in the combustion chamber of the C.F.R. engine and the occurrence of ignition at optimum values of the compression ratio was obtained by means of the temperature plug used for the experiments of this Part. Noteworthy features of the experimental results as exhibited by the graphs of Fig. 9 are stated below.

When the heptane-air mixture was correct and the plug not cooled, its temperature rose to 1020°F . when the Opt.C.R. was 5.7. The rate of oxidation on the surface of the plug sufficed to start a flame but a transition to nuclear ignition was necessary in order that maximum combustion pressure could occur at the time required for maximum power output as shown by the Λ indicator diagrams of Fig. 2.

When the plug was cooled to 610°F . to be equal to the temperature of the standard C.F.R. exhaust valve, the Opt.C.R. was 8.0. Then when it was cooled to 325°F . to be equal to the temperature of the sodium cooled exhaust valve, the Opt.C.R. was 9.0. Surface oxidation was not eliminated in either case, but the rate was too low to start ignition; the change in rates was indicated by changes in the length of the fillet which connected compression and combustion pressures.

It is shown by the graphs of Fig. 9 that when M.S. was reduced to be 10% weak, the value of Opt.C.R. remained at 8.0 while the plug temperature was 700°F . or reduced to 400°F . to be equal to that of the standard C.F.R. exhaust valve. At leaner mixtures, Opt.C.R. increased nearly in direct proportion to the decrease in M.S. The temperature attained by the uncooled plug was always higher than that of the exhaust valve as shown by the graphs of Figs. 6 and 7. The difference decreased as M.S. decreased but even with a mixture approximately 75% weak, the plug temperature was 400°F . (Fig. 6) and that of the exhaust valve 200°F . (Fig. 7). When a mixture was 10.5% weak or leaner, Opt.C.R. remained nearly constant as the temperature attained by the plug for a particular mixture was reduced by cooling to a value as low as 200°F ., as shown by the graphs of Fig. 5.

Data determined for the relation between plug temperature and Opt.C.R. when the exhaust valve was sodium cooled have been used to obtain the relation between Opt.C.R. and M.S. if the plug temperature were held constant at a temperature of 400°F ., which is 10°F . higher than the maximum attained by the valve as shown by the relevant graphs of Fig. 10. The temperature of the valve could not be measured by the T.P. method when the mixture was leaner than approximately 38%, as was the case when the exhaust valve was not cooled.

It will be seen by reference to Fig. 10 that the graphs for the relation between Opt.C.R. and M.S. nearly coincided when mixtures were 39% to 30% weak. A real separation became apparent as M.S. was increased, and with a correct mixture, Opt.C.R. was 8.9 with the sodium cooled valve at a temperature of

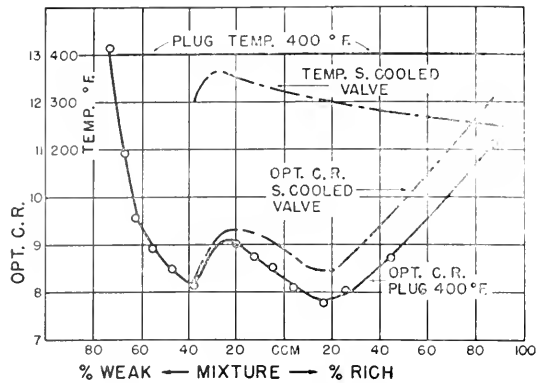


FIG. 10. Solid line graphs—Opt. compression ratios for compression ignition of heptane-air mixtures 72% weak to 90% rich when plug temperature is always 400°F, and the exhaust valve is sodium cooled.

320° F., and 8.3 with the T.P. at a temperature of 400° F. The differences increased as M.S. was increased and with a mixture 80% rich Opt.C.R. was 11.7 for the sodium cooled valve, which then attained a temperature of 260° F., and 10.7 for the temperature plug at a temperature 140° F. higher.

The relatively low heat load in the conditions of the experiments made it possible to show that the *decrease* in Opt.C.R. as M.S. was reduced over the range 25% to 40% weak is a property of a “detonating” fuel. When a nondetonating fuel such as benzene was used in the same conditions and spark timing always adjusted to the optimum value, the corresponding Opt.C.R. *increased* as M.S. was decreased from approximately correct to 40% weak, but ignition by either spark or compression did not occur at leaner mixtures.

The Relation Between the Time of Compression and the Compression Ratio Required for the Explosive Ignition of Correct Heptane-Air Mixtures

The relation is given in Table I as obtained by Tizard when using the Ricardo compression ignition machine, by Taylor *et al.* when using the machine developed in the Massachusetts Institute of Technology (10), and by the C.F.R. engine experiments of this Part when carried out with the standard uncooled exhaust valve, valve timing being taken into account.

Explosive ignition was initiated in Tizard’s experiments after a “delay

TABLE I

	Initial pressure	Initial temperature, °F.	Time of compression, sec.	C.R.
Tizard	Atmos.	140°	0.0825	6.3
Taylor <i>et al.</i>	Atmos.	150°	0.006	12.3
C.F.R. engine	53% atmos.	100°	0.061	7.9

period" of 0.25 sec. as reckoned from the completion of compression. That is, the time was three times the time of compression. The delay was 0.001 sec. approximately in the Taylor *et al.* experiments, that is, $\frac{1}{3}$ of the time of compression. Explosive ignition was initiated in the engine at approximately 5° of crank revolution after t.d.c., as shown clearly by experiments made when the T.P. was not used, Part XXI (6, Fig. 5) and Part XXV (1, Fig. 7). The delay time if reckoned from the completion of compression at t.d.c. was then 0.002 sec., which is $\frac{1}{30}$ of the time of compression although Opt.C.R. was 7.9 only. The delay time must therefore have begun during the compression stroke of the engine.

The true delay time is that required for preflame reactions to produce an igniting concentration of carbon nuclei in the gaseous mixture according to the nuclear theory as stated in Part IV (1). This statement was made in respect of the end gas in a spark ignition engine and applies only to gaseous mixtures that can thus be ignited. It is well known that spark ignition is irregular in the mixture range 20% to 25% weak. It was shown to become completely ineffective as M.S. approached 40% weak, Part XXI (6, p. 235). Further discussion will for the present be restricted accordingly.

Oxidation and decomposition reactions can occur simultaneously during compression in a carburetor engine operated as for the experiments described in this Part. It is shown by the indicator diagrams of Fig. 2 that as the plug temperature was reduced to that of the exhaust valve, the oxidation reaction on the combined surface area of the plug and valve was effective only in providing a fillet connecting compression and explosion pressures. The explosive ignition must therefore have been due to the carbon nuclei produced by a decomposition reaction. The rate of the production of carbon nuclei increases with the increase of temperature and pressure due to an increase of C.R. The concentration of nuclei per unit volume of gases mixture increases directly with increase of pressure. An explanation may thus be provided for the delay time of approximately 0.001 sec. observed by Taylor *et al.* for a correct heptane-air mixture and a C.R. of 12.3. It is possible, however, that the delay time began before compression had been completed, in view of the fact that compression time was six times that of the delay time as it was measured.

Explosive Ignition of the End Gas when Ignition is by Spark

When ignition is started by a spark or by a hot spot provided by a surface in the combustion chamber of an engine, flame is propagated in the compressed fuel-air mixture by the normal thermal process unless explosive ignition occurs in the mixture ahead of the flame front. The phenomenon is commonly described as detonation of the end gas and was observed in the experiments of this Part when a nearly correct heptane-air mixture was ignited by a hot spot provided by the temperature plug, as shown by the A indicator diagrams of Fig. 2. A similar effect was demonstrated by Taylor *et al.* when a heptane-air mixture compressed in the M.I.T. machine was ignited by a spark (10, Fig. 68).

Relevant data for the two experiments are tabulated below.

TABLE II

Method of experiment	F/A ratio	C.R.	Ignition	Approx. time of combustion of end gas
M.I.T. machine	0.066	6.8	Spark	0.3 millisecc.
C.F.R. engine	0.064	6.77	Hot spot	0.8 millisecc.

The combustion times were taken from pressure time diagrams and although the values are approximate, the longer time required for combustion of the end gas in the engine is consistent with its dilution with residual products to a greater than normal extent because the initial pressure was 53% of atmospheric. It is also to be noted that initial pressure in the M.I.T. machine was 5.5% greater than atmospheric and the mixture 3% richer than that in the engine.

The high speed photographic records taken in the course of experiments with the M.I.T. compression ignition machine show that ignition was initiated by discrete bright spots of flame. Taylor *et al.* comment on the similar bright spots observed by C. D. Miller when high speed photographs were taken of the autoignition of the end gas in an engine (9, pp. 98-143) and further on the theory of King *et al.* that nuclei of free carbon are involved in the autoignition process as shown by experiments with the hydrogen engine described in Part V (8). The theory received further support by the hydrogen engine experiments described later (in Part XXVII (7)).

It should be noted that the bright spots mentioned by Taylor *et al.* appeared prior to autoignition. The phenomenon was therefore not similar to that observed by Miller when autoignition occurred in the end gas of an engine. The bright spots which appeared in the M.I.T. experiments may well have indicated the beginning of ignition on the surface of the glass plate which was necessary for the taking of photographic records of the progress of combustion.

Detonation Pressure Waves

The temperature of a homogenous gaseous fuel - air mixture is not uniform at the end of compression even in a single stroke compression ignition machine, as mentioned by Tizard and later by Taylor *et al.* An even greater lack of uniformity would be expected in an engine because of the local heating effect of the exhaust valve. The decomposition or pyrolysis of the fuel to the extent necessary for the production of an igniting concentration of nuclei would be most advanced in the portion of the mixture in which temperature exceeded the mean value due to compression to the greatest extent. It may safely be assumed that maximum compression temperature was attained by the mixture near the exhaust valve irrespective of turbulence, when ignition was by compression as in the experiments described in this Part. When ignition is by spark the position of maximum temperature in the end gas is difficult to define because it depends on the position of the spark plug relative to that of the exhaust valve, on the characteristics of turbulence, and on the geometry of the combustion space.

Detonation in any event would occur in only that part of the mixture which is sensitive to the effect. That would be the mixture in the end gas in a spark ignition engine and the whole mixture at the end of the compression stroke in a compression ignition engine. The consequent pressure wave as it passed through the remainder of the mixture would raise its somewhat lower temperature to the degree required to start additional pressure waves. There would thus be a complication of pressure waves which would be increased by reflections from the walls of the combustion chamber and by the impact of one wave upon another. It is not surprising therefore that no demarcation of a detonation wave was shown by the flame photographs of Taylor *et al.* although they were taken at the rate of 10 frames per millisecond or by the rate of pressure change diagrams taken in the course of experiments described in this Part. However in all of these diagrams the gas vibrations which followed detonation were shown clearly although their frequency as measured from enlargements was 5.0 per millisecond approximately.

Nuclei of Ignition

Detonation that occurs in the end gas when fuel air mixtures are ignited by spark is, in accordance with the nuclear theory of ignition as stated in Part IV (1), due to the igniting effect of finely divided carbon derived from decomposition or pyrolysis of the fuel. This carbon accounts for the brilliant white flame of detonating combustion. The flame is blue in operating condition in which detonation does not occur unless the mixture is over rich and vaporization is not complete. Carbon not consumed in the flame appears as a residue on surfaces in the combustion chamber and as black smoke in the exhaust.

When a spark plug was not used, as for the experiments with heptane air mixtures described in this Part, and C.R. was raised to the value required for ignition with maximum power output, detonation began in part of the whole gaseous mixture, as there was then no end gas. The characteristics of detonating combustion were similar to those described for spark ignition when, as with spark ignition, mixtures were richer than 25% weak.

Mixture strength appears to have a critical value when it is 25% weak. Then as it is increased from that value, residues of finely divided carbon tend to appear on surfaces in the combustion chamber when detonation follows spark or compression ignition. As M.S. decreases from 25% weak, spark ignition tends to become of nil effect. Ignition by compression remains effective but residues of the nuclei of ignition appear to be a mixture of carbon and resin. A corresponding increase in the inflammability of the nuclei of ignition was indicated by a decrease in optimum C.R. as mixture strength was reduced from 25% to 40% weak. Then as mixture strength was further reduced the flame of combustion ceased to be white and became a brilliant blue.

Aldehydes were noticeable in the exhaust as the mixture became leaner than 25% weak. The accompanying increase in the inflammability of carbon nuclei may be due to their absorption and condensation of a particular variety of aldehyde. However, residues of resinous substance increased in quantity when rate of aldehyde formation increased as mixtures leaner than 10% weak were

used, as described in Part XXIV (3, p. 235). Corresponding values of Opt.C.R. increased and flame became a bright blue. This indicated that nuclei of ignition no longer contained carbon. The combustion of these lean mixtures occurred in two stages and was nearly silent.

Experiments carried out especially to determine the role of aldehydes in the compression ignition of mixture leaner than can be ignited by a spark will be described in the second paper on the subject of this Part.

ACKNOWLEDGMENTS

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THE OXIDATION, DECOMPOSITION, IGNITION, AND
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XXX. THE HYDROGEN ENGINE AND DETONATION OF THE END GAS BY
THE IGNITING EFFECT OF CARBON NUCLEI FORMED BY PYROLYSIS OF
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By R. O. KING² AND S. V. HAYES³

ABSTRACT

Experiments with a C.F.R. spark ignition engine were carried out at compression ratios of 13 : 1 and lower. It was found that ignition and detonation of the mixture ahead of the flame front was due to its impregnation with finely divided carbon produced by the pyrolysis of the vapor of lubricating oil. The carbon accumulated on surfaces until in part dispersed into the hydrogen-air mixture by the entering turbulence. The carbon in the aerosol thus formed ignited at the relatively high temperature and pressure attained by the end gas in the conditions of the experiments. The onset of the consequent detonation and its severity at a particular engine speed was found to be dependent upon the factors of compression ratio, mixture strength, the initial compression temperature and that of the jacket coolant, the nature of the lubricating oil, and the rate at which it passed the piston into the combustion chamber or was supplied as an additive. Thus in the final experiment for which prevaporized cetane was used as an additive the shock of the accompanying detonation pressure waves was so great that the cylinder broke loose from the crank case because of the failure of the retaining casting.

INTRODUCTION

It was shown by experiments with hydrogen as the fuel for a C.F.R. Otto cycle engine (Part XXVII (1)), that preignition did not occur at a compression ratio of 10 : 1 when the exhaust valve was sodium-cooled and the spark plug was a cool running type. These experiments were carried out at engine speeds ranging from 900 to 1800 r.p.m. The jacket coolant was maintained at 100°F. and the air supply at 65°F. Mixtures ranging from 70% weak to 60% rich were used without the occurrence of detonation.

When the compression ratio was raised to 12 : 1, the top piston ring overlapped the three spark plug holes in the cylinder wall and lubricating oil passed into the combustion chamber at the positions of the holes at a rate greater than normal, as shown by the accumulation of soot on adjacent surfaces of the piston crown. Slight preignition then occurred infrequently when the engine was operated at 1800 r.p.m., although the jacket coolant had been reduced to 65° F. as a precautionary measure. When lower speeds at 1500 and 1200 r.p.m. were used, the frequency of preignition increased and backfiring as well as what appeared to be detonation occurred occasionally as mixture strength was increased to the correct value. These effects were avoided by allowing the engine to run for a few minutes on a weak

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mixture before using a correct or rich mixture in order to burn off excess carbon.

The experiments of this Part were carried out for the purpose of determining the operating conditions responsible for the occurrence of preignition and for detonation of the end gas by the igniting effect of carbon nuclei arising from pyrolysis of the vapor of lubricating oil passing the piston or supplied as an additive.

EXPERIMENTAL ARRANGEMENTS

The experiments were carried out with the C.F.R.-FI engine that had been used for those described in Part XXVII (1). The exhaust valve was sodium-cooled. The cast iron piston was fitted with four pressure rings and one oil scraper ring. Ignition was by a cool variety of spark plug in the standard position but spark was not required after the exhaust valve had attained the requisite temperature. The temperature of the oil in the crank case was maintained at 110° F. The methods of regulating engine and mixture temperature and of metering rates of supply of air and hydrogen were as used for the experiments described in Part XXVII. Engine speed was maintained at 1200 r.p.m. except for the experiments described in Section IV. Mixtures are described as per cent weak or rich according to the percentage by which the hydrogen to air volume ratio is less or more than that required for a chemically correct mixture.

Oils Used as Lubricants or as Additives

Oils described as P.30 and P.10 were from a paraffin base crude and were graded by the supplier as S.A.E. 30 and S.A.E. 10 respectively. They were free of oxidation inhibitors or detergents. A synthetic oil, L.B. 300 X, is described as S.300. Cetane, $C_{16}H_{34}$, as obtained from the Eastman Kodak Co., was used as an additive only.

The terms "compression ratio" and "mixture strength" are abbreviated in subsequent text, as convenient, to C.R. and M.S. respectively, and compression ratios are stated as single numbers.

I. PRELIMINARY EXPERIMENTS

Compression ratios of 13.0 and 12.3 were used. Lubricating oil therefore passed the piston at a greater than normal rate at the positions of the three spark plug holes in the cylinder wall as was shown by the experiments of Part XXVII. Oils S.300 and P.10 were used when the C.R. was 13.0 and the jacket coolant maintained at 55° F. Oil S.300 only was used when the C.R. was 12.3 and the jacket coolant was raised to a temperature of 110° F.

Experimental Results, C.R. 13.0

Jacket Coolant 55° F., Mixture Supplied at 70° F., Speed 1200 r.p.m.

The experiment was started with a mixture 20% weak and the engine operated for 15 min. with spark timing adjusted to the optimum value. M.S. was then gradually increased and spark timing always adjusted to the

corresponding optimum until the engine continued to run without spark ignition. The crank case was always cleared of used oil and washed before it was filled to the standard level with a different variety. It appeared however that considerable "blow by" occurred at compression ratios used for the experiments. Thus after an oil had been used for 15 hr. running time it was found to have become blackened, presumably by impregnation with the carbon that had been formed in the combustion chamber and not retained in the standard oil filter of the engine; as a matter of some interest an experiment was carried out with oil S.300 that had been used for the running time mentioned. Experimental results are tabulated below.

TABLE I

Oil in crank case	M.S. required for detonation
S.300 fresh	Correct
S.300 used for 15 hr.	4.5% weak
P.10 fresh	8.0% weak

The results indicate that the vapor of oil S.300 is more resistant to pyrolysis than that of the paraffin base oil P.10 and that resistance diminishes as the oil becomes impregnated with the finely divided carbon.

Experimental Results, C.R. 12.3

Jacket Coolant 140° F., Mixture Supply 60° F., Speed 1200 r.p.m.

The crank case was drained of used oil and washed before it was filled to the standard level with fresh oil, S.300. Vaporization of oil deposited on surfaces in the combustion chamber was promoted by raising the temperature of the jacket coolant to 140° F. The experiment was started, as before, with a mixture 20% weak, which after 15 min. running time, was gradually increased while spark timing was adjusted to corresponding optimum values. The engine continued to run without spark ignition when M.S. had been increased to the correct value. Four indicator diagrams were then taken by means of a Photocon capacitance type of pressure pickup, the associated amplifier, and a Dumont oscilloscope. The diagrams are reproduced as Fig. 1. They show that, although a spark was not used, detonation occurred whilst combustion pressure was rising. The initiation of combustion must therefore have been due to the attainment of an igniting temperature by the surface of maximum temperature. This was necessarily that of the exhaust valve because the spark plug was an exceptionally cool variety and the detonation must have occurred in the end gas. The timing of surface ignition could not be regulated in conditions of a fixed C.R. and engine speed and was therefore somewhat irregular. The diagrams show that detonation occurred before t.d.c. in the circumstances. The engine continued to run but with power output reduced by approximately 30%. However the shock of detonation pressure waves occurring before t.d.c. was so severe that the experiment was discontinued after indicator diagrams had been taken.

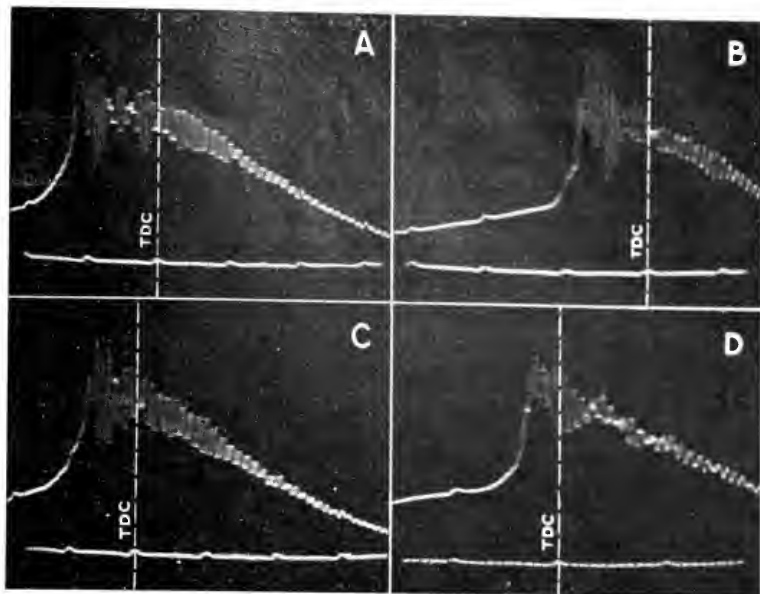


FIG. 1. Pressure-time diagrams, C.R. 12.3, 1200 r.p.m. Oil S.300 in crank case, jacket coolant 140° F., correct mixture supply at 60° F.

II. LUBRICATING OIL ADDED TO THE HYDROGEN-AIR MIXTURE AS A LIQUID

The experiments were carried out with a C.R. of 10.0 in order that the top piston ring should not lose its bearing on the cylinder wall at the spark plug holes. Lubricating oil from the crank case then passed the piston into the combustion chamber at the relatively low rate consequent on the cylinder and piston having been maintained in the conditions specified for the A.S.T.M.-C.F.R. method of knock rating.

Combustion of the vapor of oil added to the hydrogen air mixture would be expected to yield an increase in power output. The rate of oil addition was therefore limited to 30 cc. per hr. This is equivalent to 1/70th of a drop of warm oil per cycle. A Bosch fuel injection system was tried but failed to operate until rate of oil supply was greater than 70 cc. per hr. It was then found that the Cox sampling device* could be adapted to deliver oil to the entering hydrogen-air mixture at suitable rates. This device is designed to take a sample of gas from any part of the engine cycle during a period of 1.0 millisecond. The direction of operation was reversed and lubricating oil injected into the cylinder during the induction stroke in order that it might be dispersed into the gaseous mixture by the random turbulence created at the inlet valve. It appeared however that the oil was deposited on the cylinder wall by the turbulence. Thus it was in the same state as that passing

*The device was supplied by Commercial Research Laboratory Inc., 20 Barlett Avenue, Detroit 3, Michigan.

into the combustion space from the crank case. Many experiments were carried out but results of special interest were not obtained.

The temperature of surfaces in the combustion chamber was then increased by raising that of the jacket coolant to 212° F. The rate of vaporization of oil deposits was thus increased and distribution of the vapor in the gaseous mixture was promoted by using a shrouded inlet valve to create a swirl in it. An experiment was carried out by the method described in Section I and when M.S. was increased to be 20% weak the engine ran without spark ignition but the timing of surface ignition as shown by the oscilloscope was extremely irregular. When nuclear ignition of the end gas occurred near t.d.c. the detonation shock wave was of great violence and the experiment ended when the Draper-Li pressure pickup, rated at 2000 lb. per sq. in., was crushed and the bronze bushing of the big end bearing was deformed.

III. THE DETONATION OF HYDROGEN-AIR MIXTURES BY CARBON NUCLEI DERIVED FROM LUBRICATING OIL AS SHOWN BY LIGHT INTENSITY DIAGRAMS

The light emitted by hydrogen burning in air is too low in intensity for photographic recording, irrespective of its concentration in the air. The light emitted by the burning of the vapor of lubricating oil in a homogeneous mixture with air is also too low in intensity for photographic recording when the concentration of air in the mixture is greater than required for complete combustion. The vapor of lubricating oil did not however form a homogeneous mixture with the gaseous mixture in the conditions of the experiments described in Section II and soot was deposited on surfaces in contact with flame even when the concentration of oxygen was in excess of that required for complete combustion. It was indicated by experiments described in Part XXVII (1) that the deposits built up as running continued until they were in part dispersed into the gaseous mixture by turbulence. Detonation would be caused by the soot becoming incandescent or pyrophoric at the temperature attained by the end gas, and light emission might be of sufficient intensity for photographic recording. Experiments carried out accordingly are described below.

Arrangements for Light Intensity Experiments

The viewing window, a short length of polished pyrex rod, occupied one of the spare holes in the cylinder wall. Light from the window was received by a photoelectric multiplier which provided a light intensity - time diagram on the screen of a dual-beam Dumont oscilloscope. The necessary spark ignition was by a cool plug in the standard position. The second spare hole was occupied by a "Sunbury" pressure pickup which provided a rate of pressure change - time diagram on the oscilloscope screen simultaneously with the light intensity - time diagram.

Conditions of Engine Operation

The hydrogen-air mixture was 55% weak. Engine speed was maintained at 900 r.p.m. by adjustment of load. The compression ratio was fixed at 10.0.

The temperature of the jacket was 212°F . and that of the mixture 70°F . A shrouded inlet valve was used to produce a swirl in the mixture. The crank case was cleared of used oil and then filled to the standard level with fresh S.300 oil. Oil P.30 as an additive was supplied by the Cox sampling device at the rate of 22.0 cc./hr.

Light Intensity and Rate of Pressure Change Diagrams

Photographs of diagrams which appeared simultaneously on the screen of the dual beam oscilloscope are reproduced as Fig. 2. The upper and lower horizontal traces on the diagrams are for part of the cycle in which there was no combustion. The lower trace is therefore for zero rate of pressure change

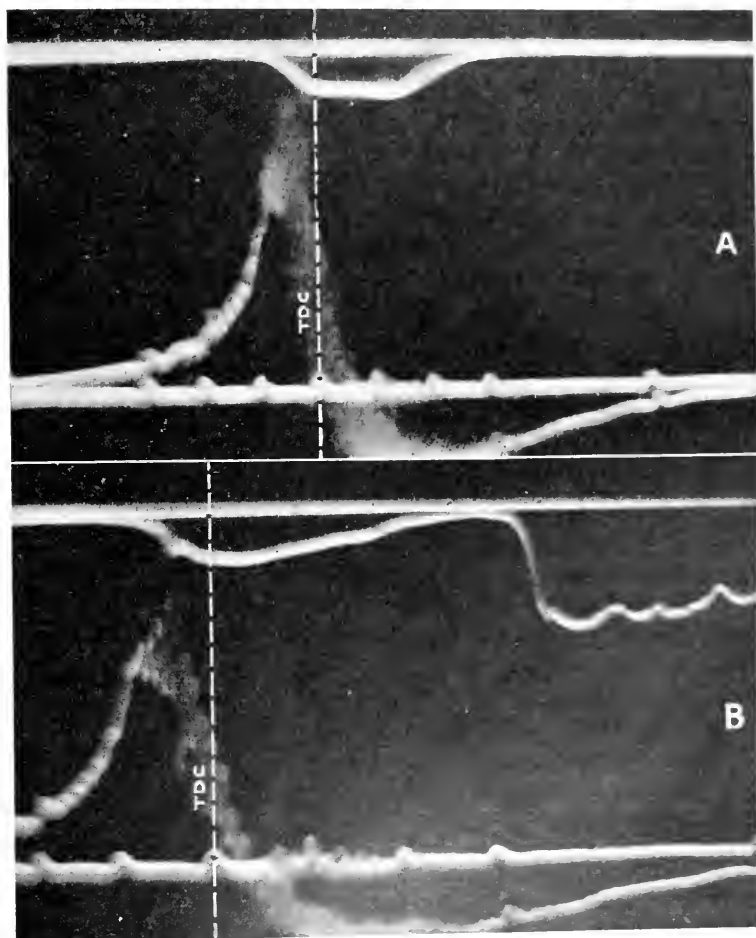


FIG. 2. Light intensity and rate of pressure change diagrams taken simultaneously C.R., 10.0. Oil S.300 in crank case, jacket coolant 212°F ., speed 900 r.p.m., mixture 55% weak at 70°F .

A. No additive.

B. Oil P.30 added by Cox device at 22 cc./hr.

and the upper for zero light intensity. The light intensity trace extends down from the zero trace because a negative potential from the photoelectric multiplier was applied to the magnetizing coil of the related beam of the oscilloscope and the circuit to the multiplier completed through earth. The small "blips" on the lower trace are 10° of crank revolution apart and represent time intervals of 1.85 milliseconds at the engine speed 900 r.p.m., in respect of the upper as well as the lower horizontal trace. The blip at t.d.c. is marked by a broken vertical line. Combustion of the hydrogen is shown to be substantially complete at the time in degrees of crank revolution indicated by the intersection of the rate of pressure change trace with the horizontal trace for zero rate of pressure change. It is shown by both light intensity diagrams that the luminosity due to incandescent carbon particles appeared late in the combustion period and the rate of pressure change diagrams show that detonation then occurred.

Diagrams A.—These were taken before lubricating oil was supplied as an additive. The light intensity shown by the relevant diagram was then due to the incandescence of carbon particles that had been formed by pyrolysis of the vapor of oil S.300 that had passed the piston into the combustion chamber. The diagrams show luminosity beginning at 10° before t.d.c. with faint detonation pressure waves accompanying the igniting effect of the carbon particles. Combustion of the hydrogen was then well advanced and was substantially completed at approximately 5° after t.d.c. but luminosity due to the incandescence of free carbon continued until 15° after t.d.c. That is for 10° of crank revolution after combustion of the hydrogen had been completed.

Diagrams B.—These were taken while the paraffin base oil was supplied by the Cox sampling device as an additive, at the rate of 22 cc./hr. The diagrams show that luminosity appeared, as in the diagrams A, at approximately 10° before t.d.c. but the accompanying detonation pressure waves are more clearly defined. The pressure waves were not of sufficient energy to cause knock that was easily audible. Luminosity due to the incandescence of free carbon continued until it became zero at 45° after t.d.c., that is, for 40° of crank revolution after combustion of the hydrogen had been completed. Incandescence of free carbon then recurred with the emission of a relatively high level of light intensity which diminished slowly during the remaining time interval shown on the diagrams. The hydrogen-air mixture always contained some small proportion of oil vapor and the small pressure changes shown by the rate of pressure change diagrams before the occurrence of detonation and the later fuzziness of the diagrams are attributed to partial burning of the vapor.

The Recurrence of Luminosity

The finely divided carbon or soot formed by pyrolysis of the vapor of lubricating oil was of the nature of carbon black. It is known that the particle size in that material varies to an extent depending on the method of pyrolysis and the nature of the substance from which it was procured, and that the

freshly formed carbon possesses in a remarkable degree the power of absorbing gases. These characteristics may afford an explanation for the recurrence of luminosity during the expansion stroke of the engine, especially in view of the relatively large concentration of free oxygen then available because the hydrogen-air mixture supplied to the engine was 55% weak.

Oil S.300 passed the piston at the minimum practicable rate and it may be assumed that the carbon produced by pyrolysis was composed of extremely fine particles. Light was emitted for 15° of the expansion stroke only as shown by diagrams A and as there was no recurrence of luminosity it appears that all of the carbon was consumed by the oxygen then available.

The carbon produced by pyrolysis of hydrocarbons is known to contain both fine and coarse particles, thus when oil P.30 was used as an additive the burning of the fine particles and those produced by pyrolysis of oil S.300 passing the piston would account for the emission of light during 25° of the expansion stroke as shown by diagrams B. The subsequent occurrence of luminosity with a relatively high light intensity may be attributed to the burning of the coarser particles initiated by the adsorbed oxygen and sustained by the available free oxygen. The rate at which oil was vaporized was far from constant, when it was supplied as a liquid additive, and in some cases light emission was continuous although of variable intensity during the part of the expansion stroke shown on the diagrams.

IV. THE PREVAPORIZATION OF ADDITIVES AND EXPERIMENTS WITH CETANE

Experiments described in preceding sections demonstrated that the finely divided carbon responsible for detonation in the end gas was provided by the pyrolysis of the *vapor* of the lubricating oil. Vaporization involves a time factor, as represented by engine speed; thus whatever the rate at which oil passes the piston into the combustion chamber the proportion vaporized prior to spark ignition, at a particular speed, is not increased to a significant extent except by raising the temperature of surfaces to which the oil adheres as a liquid and thus inviting the occurrence of preignition due to the temperature attained by the exhaust valve. Thus it appeared that oil or cetane when used as an additive should be vaporized immediately prior to admission through the inlet valve, if results of an enhanced significance were to be obtained. A method of vaporization was therefore devised and used for experiments described in this Section.

The Methods of Vaporizing and Metering Small Rates of Supply of Liquid Additives

The vaporizing device and its arrangement for the discharge of vapor into the well of the inlet valve are shown by Fig. 3. The device comprises three concentric tubes. The outer one is of mild steel with an inside diameter of 0.30 in., and a perforation is provided in the blank lower end through which vapor of the additive is discharged. Within the outer tube is a concentric thin-walled steel tube having an outside diameter of 0.25 in. The annulus

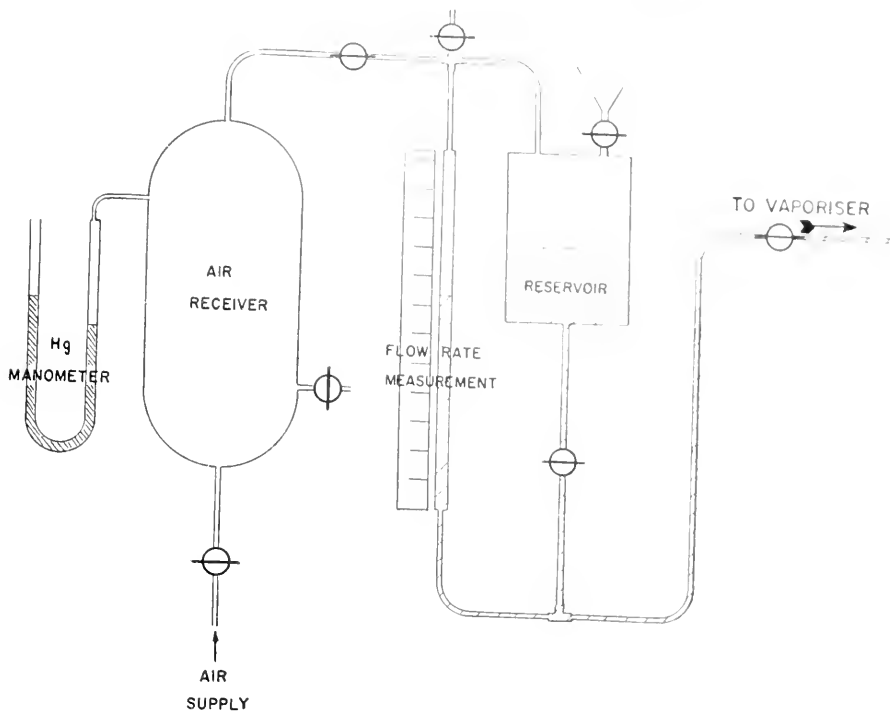


FIG. 4. Device for the supply of liquid additives to the vaporizer at measured rates.

additive in a graduated glass tube having an inside diameter of 1.0 mm. It was possible to measure accurately rates of additive supply as low as 3.0 cc./hr., and complete vaporization of the additive was obtainable with rates of supply greater than were required for experiment. The heating current was always regulated to be little greater than required for complete vaporization of the additive. The device was found to be suitable for the vaporization of lubricating oils as well as for additives with a unique boiling point. The results obtained when cetane was used are presently described. Those obtained when lubricating oils were prevaporized will be described in a subsequent paper.

Conditions Used for Experiments with Prevaporized Additives

Preliminary experiments with cetane demonstrated that detonation shock became extremely severe as mixture strength approached the correct value, and in consequence charge density was reduced by throttling to 61% of normal. Otherwise the conditions of experiment were as follows: compression ratio 10.0, engine speed 900 r.p.m., mixture temperature 110° F., and jacket coolant 212° F. Spark ignition, when used, was by a cool plug. Cetane was supplied to the vaporizer at the rate of 30 cc./hr. A Photocon pressure pickup with associated electronic equipment was used to obtain pressure-time diagrams.

Experimental Results with Cetane as an Additive

The engine was warmed up by running with spark ignition for 15 min. on a mixture 50% weak, with oil S.300 in the crank case. M.S. was then gradually increased and spark timing always adjusted to corresponding optimum values. A considerable degree of detonation was observed when M.S. had been increased to be 15% weak. Pressure-time diagrams were then taken at two-minute intervals for a period of eight minutes, and have been reproduced as Fig. 5 with t.d.c., marked by a vertical broken line. They show

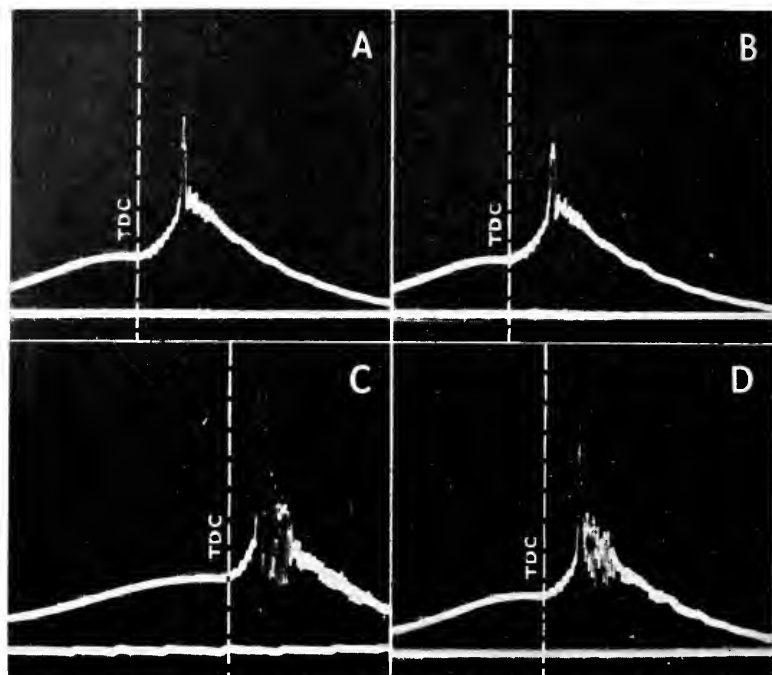


FIG. 5. Pressure-time diagrams taken at 2-min. intervals until spark ignition was replaced by surface ignition. C.R. 10, speed 900 r.p.m., jacket coolant 212° F., mixture 110° F. and 15% weak.

little variation in the time of occurrence of detonation, which always occurred after t.d.c., but show that the volume of end gas in which the effect occurred tended to increase. There was a corresponding increase in the amplitude of the gas vibrations which follow detonation pressure waves, and the engine continued to run when the spark was switched off.

Cetane was then supplied to the vaporizer at the rate of 30 cc./hr., and the four pressure-time diagrams reproduced as Fig. 6 were taken at half-minute intervals. They show that nuclear ignition accompanied by detonation pressure waves continued to occur in the end gas, and as combustion was not initiated by a spark it must have been initiated on the attainment of the requisite temperature by the exhaust valve, which provided the surface of maximum temperature in the combustion chamber. Thus the diagrams show that ignition timing was much less regular than when combustion was initiated by a spark, as would be expected.

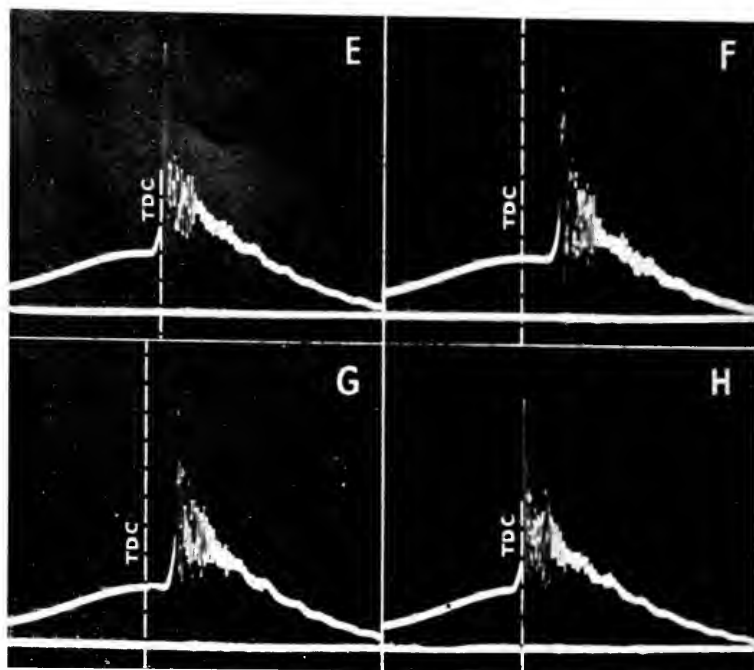


FIG. 6. Running continued with surface ignition and with addition of 30 cc. hr. of cetane prevaporized. Pressure-time diagrams taken at $\frac{1}{2}$ min. intervals until cylinder broke loose from crank case.

It is shown by the last diagram taken that nuclear ignition accompanied by detonation pressure waves of large amplitude had occurred at t.d.c. The engine was unable to tolerate the consequent shock and the cylinder broke loose from the crank case because of the fracture of the retaining casting.

CONCLUSION

Experiments described in Part V (2) and Part XXVII (1) demonstrated that if an experiment were started with a clean combustion chamber, detonation did not occur until a deposit of soot arising from pyrolysis of lubricating oil vapor had built up on surfaces to such an extent that it was in part carried into the hydrogen-air mixture by turbulence. The consequent detonation occurred irregularly and a residue of soot always remained on surfaces in the combustion chamber.

It was concluded that detonation would not be dependent on a build-up of surface deposits of soot if the hydrogen-air mixture entering the cylinder carried the vapor of oil. The vaporizer described in Section IV *ante* was designed accordingly. Cetane, a standard fuel oil for the Diesel engine, was selected for experiments because of its unique boiling point, 549° F. The vapor was mixed with the hydrogen-air mixture by being ejected into the well of the inlet valve but it appeared that it formed a fog in the relatively cool gaseous mixture and that some might condense on surfaces before being dissipated by the heat of compression. The temperatures of surfaces were

therefore raised by maintaining the jacket coolant at 212° F. and the hydrogen-air mixture supply was maintained at 110° F. The mixture was 15% weak, engine speed 1200 r.p.m. Spark ignition was necessary and timing was adjusted to the optimum value, 3° in advance of t.d.c.

It is shown by the diagrams of Fig. 5 that combustion pressure rise began at t.d.c. approximately, and continued in the normal manner for about 5° of crank revolution. Detonation accompanied with large scale pressure waves then occurred in the end gas. The diagrams show that normal combustion and the subsequent detonation occurred with a high degree of regularity. They show also the small scale pressure waves known to follow spark ignition.

When the vapor of cetane was added to the mixture, running continued with spark ignition switched off. Thus it appeared that the temperature attained by the exhaust valve sufficed for the ignition. It is shown by the diagrams of Fig. 6 that combustion then proceeded in the normal manner for a brief and variable time interval before the occurrence of detonation in a corresponding volume of end gas. Thus it is shown by diagram E that detonation had occurred at t.d.c. in nearly the whole of the mixture, by diagrams F and G that detonation occurred after an appreciable interval of normal combustion, at from 5° to 10° after t.d.c., by diagram H, that detonation occurred again at t.d.c. in substantially the whole mixture. The diagrams of Fig. 6 were taken during a running period of two minutes. Thus combustion occurred 900 times while the hydrogen-air contained the vapor of cetane in the extremely small concentration provided by the supply of the liquid to the vaporizer at the rate of 30 cc./hr., i.e., 0.0011 cc. per cycle. The diagrams show that detonation may have occurred at t.d.c. in half of the combustion periods. It is not surprising therefore that the cylinder broke loose from the crank case after two minutes of running. The damage to the engine would have been regretted had it not provided a striking illustration of nuclear ignition of the end gas and its consequent detonation.

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